

BIODEGRADABLE RESIN FILM AND MOLDED OBJECT**Publication number:** JP7247374**Publication date:** 1995-09-26**Inventor:** KOTANI KOZO; KAWAKITA TOSHIO; SAKATANI TAIICHI;
KURODA TOSHIYA**Applicant:** SUMITOMO CHEMICAL CO**Classification:****- International:** C08J5/18; B32B9/00; B32B27/18; C08K3/00; C08K7/00;
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C08J5/18; B32B9/00; B32B27/18; C08K3/00; C08K7/00;
C08L3/02; C08L29/04; C08L67/04; C08L101/10; C09C1/42**- European:****Application number:** JP19950009042 19950124**Priority number(s):** JP19950009042 19950124; JP19940006013 19940124**Report a data error here****Abstract of JP7247374**

PURPOSE:To provide a biodegradable resin film which has high barrier properties while retaining biodegradability by forming at least one layer of a resin composition comprising a biodegradable resin having a high hydrogen-bond content and a specific inorganic compound having a layered structure. **CONSTITUTION:**This film has at least one layer of a resin composition (a) comprising a biodegradable resin (b) having a high hydrogen-bond content and an inorganic compound (c) having a layered structure. In the resin (b), the content of groups linked through a hydrogen bond is 20-60wt.%. Examples of the resin (b) include poly(vinyl alcohol), polysaccharides, and derivatives thereof. The compound (c) has a particle diameter of 5Xm or smaller and an aspect ratio of 50-5,000. Examples thereof include clayey minerals and phosphoric acid salt derivatives. Although the (b) to (c) ratio is not particularly limited, it is preferably 5/95-90/10 by volume. The composition (a) may be produced by dispersing an inorganic compound having a layered structure into a dispersion medium to swell and cleave the compound, adding the dispersion to the resin (b), and removing the medium. The film has an oxygen permeability (30 deg.C, 60%RH) of 0.2cc/m<2>.day.atm or lower.

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(54) 【発明の名称】 生分解性樹脂フィルムおよび成形品

(57) 【要約】

【目的】 生分解性のガスバリアフィルムを提供すること。

【構成】 粒径が5 μ m以下、アスペクト比が50以上5000以下の無機層状化合物と生分解性樹脂を含む層を少なくとも1層有する生分解性フィルム。

【特許請求の範囲】

【請求項 1】生分解性高水素結合性樹脂と粒径が $5\mu\text{m}$ 以下、アスペクト比が 50 以上 5000 以下の無機層状化合物を含む樹脂組成物からなる層を少なくとも 1 層有する生分解性樹脂フィルム。

【請求項 2】生分解性高水素結合性樹脂がポリビニルアルコールまたは多糖類を主成分とする樹脂であることを特徴とする請求項 1 記載の生分解性樹脂フィルム。

【請求項 3】無機層状化合物が、溶媒に膨潤・へき開することを特徴とする請求項 1 記載の生分解性樹脂フィルム。

【請求項 4】無機層状化合物が、膨潤性をもつ粘土鉱物であることを特徴とする請求項 1 記載の生分解性樹脂フィルム。

【請求項 5】無機層状化合物のアスペクト比が、200～3000であることを特徴とする請求項 1 に記載の生分解性樹脂フィルム。

【請求項 6】少なくとも 1 層が多糖類およびその誘導体を主成分とする樹脂である請求項 1 に記載の生分解性樹脂フィルム。

【請求項 7】少なくとも 1 層が微生物産生ポリエステルを主成分とする樹脂である請求項 1 に記載の生分解性樹脂フィルム。

【請求項 8】少なくとも 1 層が生分解性ポリエステルを主成分とする樹脂である請求項 1 に記載の生分解性樹脂フィルム。

【請求項 9】請求項 1～8 のいずれか 1 項に記載の生分解性樹脂からなる成形品。

【請求項 10】 30°C 、60%RH 下での酸素透過度が $0.2\text{cc}/\text{m}^2\cdot\text{day}\cdot\text{atm}$ 以下であることを特徴とする請求項 1～9 のいずれか 1 項に記載のフィルムまたは成形品。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、ガスバリア性と生分解性に優れたフィルムおよび成形品に関するものである。

【0002】

【従来の技術】包装に求められる機能は多岐にわたり、機械的保護性、安全性、衛生性、作業性、商品性（透明性、印刷性、ヒートシール性）、便利性、経済性などがあげられるが、内容物保護性としての各種ガスバリア性は食品の保存性を左右する大切な性質であり、流通形態、包装技術の多様化、添加物規制、嗜好の変化などにより、その必要はますます大きくなっている。そして、それは一般プラスチック材料の弱点でもあった。食品の変質要因は酸素・光・熱・水分であり、とりわけ酸素はその起因物質となっている。バリア材はこれを有効に遮断すると同時にガス充填や真空包装などの食品の変質を制御する手段にとってもなくてはならない材料となる。また、酸素ガスだけでなく各種のガス、有機溶剤蒸気、

香気などのバリア機能により、炭酸ガス飲料容器や防錆、防臭、昇華防止、化粧品、農薬、医療の分野にも大変有効に利用されている。

【0003】熱可塑性樹脂よりなるフィルムの中で、特に配向されたポリプロピレン、ポリエステル、ポリアミド等のフィルムは、優れた力学的性質や、耐熱性、透明性などを有し広く包装材料として用いられている。しかし、これらのフィルムを食品包装用として用いる場合には、その気体透過性が大きすぎることから酸素遮断性が不十分であり、酸化劣化による場合や好気性微生物による場合など内容物の変質を招きや易く、通常は他の酸素遮断性の良い膜層を積層するなどの方法がとられている場合が多い。その最も代表的な手段としてはアルミニウムなどの金属箔をラミネートしたり、それら金属を熱可塑性樹脂フィルム表面に蒸着する方法が用いられ、優れた気体遮断性、特に酸素遮断性が有効に活用されている。

【0004】従来より、酸素透過性の小さな透明プラスチック素材も種々知られており、例えば、ポリビニルアルコールやポリエチレンビニルアルコール共重合体およびポリ塩化ビニリデン系樹脂から成るフィルム等があるものの、缶詰、瓶詰に用いられる金属やガラス素材は酸素透過度がほとんど零であるのに対して、これらプラスチック素材は未だ無視できない程度の酸素を透過するのである。

【0005】ガスバリア性発現の方法として、樹脂中への扁平形態の無機物の分散方法があり、これに関して特許中にいくつかの実例が見られる。例えば、特開昭 62-148532 号公報においては、透明な熱可塑性樹脂と、粒径が $500\mu\text{m}$ 以下で、アスペクト比が 5 以上の薄片状マイカより成る塗工液組成物を離型性基材上に塗工、乾燥し、次いで基材上から剥離する製造方法が記載されている。また、特開昭 64-043554 号公報においては、薄片状マイカとしてマスコバイト (KA13(AlSi3010)(OH)₂：非膨潤型マイカ) を使用し、粒径は 325 メッシュ ($44\mu\text{m}$) より小さく、アスペクト比は 20～140 の範囲が開示されている。さらに、特開平 03-093542 号公報においては、シリル基含有変性ポリビニルアルコールと合成ヘクトライト (ラポナイト XLS；日本シリカ工業製) とが重量比で 50：50 である塗工組成物を、二軸延伸ポリエチレンテレフタレート (OPET) 上に塗布し、乾燥させ、熱処理 ($130\sim 150^{\circ}\text{C}$) する方法が開示されている。

【0006】また、包装材料は使い捨て用途であるため、近年の地球環境問題への関心の高まりと共に、生分解性の付与が言われつつある。

【0007】

【発明が解決しようとする課題】しかしながら、現状ではいまだ高いガスバリア性と生分解性をあわせ持つ材料は市場に供給されていない。

【0008】本発明の目的は、上記の課題を解決しようとするものであり、これまでにないハイレベルの酸素遮断性を有しかつ生分解性である包装用フィルム、成形品を提供することにある。

【0009】

【課題を解決するための手段】本発明者らはガスバリア性材料について、長年研究を続けてきた。その結果、生分解性高水素結合性樹脂と粒径が $5\mu\text{m}$ 以下、アスペクト比が50以上5000以下の無機層状化合物を含む樹脂組成物からなる層を少なくとも1層有する生分解性樹脂フィルムが著しく優れたガスバリア性を発現しながらなおかつ生分解性であることを見だし、本発明を完成するに至った。

【0010】すなわち本発明は、生分解性高水素結合性樹脂と粒径が $5\mu\text{m}$ 以下、アスペクト比が50以上5000以下の無機層状化合物を含む樹脂組成物からなる層を少なくとも1層有する生分解性樹脂フィルムおよび成形品に関するものである。

【0011】本発明において用いられる生分解性高水素結合性樹脂は、樹脂単位重量当りの水素結合性基の重量百分率が20%~60%の割合を満足し、かつ生分解性であるものである。水素結合性基としては水酸基、アミノ基、チオール基などが挙げられる。例としては、ポリビニルアルコールや多糖類およびその誘導体がある。

【0012】本発明の無機層状化合物含有層に用いられるポリビニルアルコールとは、ビニルアルコールのモノマー単位を主成分として有するポリマーである。このような「ポリビニルアルコール」としては、例えば、酢酸ビニル重合体の酢酸エステル部分を加水分解ないしエステル交換（けん化）して得られるポリマー（正確にはビニルアルコールと酢酸ビニルの共重合体となったもの）や、トリフルオロ酢酸ビニル重合体、ギ酸ビニル重合体、ピバリン酸ビニル重合体、 α -ブチルビニルエーテル重合体、トリメチルシリルビニルエーテル重合体等をけん化して得られるポリマーがあげられる（「ポリビニルアルコール」の詳細については、例えば、ポパール会編、「PVAの世界」、1992年、（株）高分子刊行会；長野ら、ポパール、1981年、（株）高分子刊行会を参照することができる）。ポリビニルアルコールにおける「けん化」の程度はモル百分率で70%以上が好ましく、85%以上のものがさらに好ましく、98%以上のいわゆる完全けん化品がさらに好ましい。また、重合度は100以上5000以下が好ましい（さらには、200以上3000以下が好ましい）。

【0013】本発明において用いられる多糖類およびその誘導体とは、種々の単糖類の縮重合によって生体系で合成される生体高分子およびそれらをもとに化学修飾したものが含まれる。たとえば、セルロースおよびヒドロキシメチルセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロースなどのセルロース誘導体、

アミロース、アミロペクチン、プルラン、カードラン、ゼンタン、キチン、キトサン、などが挙げられる。

【0014】本発明に用いられる無機層状化合物とは、単位結晶層が互いに積み重なって層状構造を有している無機化合物をいう。換言すれば、「層状化合物」とは、層状構造を有する化合物ないし物質であり、「層状構造」とは、原子が共有結合等によって強く結合して密に配列した面が、ファンデルワールス力等の弱い結合力によって平行に積み重なった構造をいう。本発明に使用可能な「無機層状化合物」は後述する方法により測定したアスペクト比が50以上5000以下で粒径が $5\mu\text{m}$ 以下であるものならば特に限定されない。ガスバリア性の点からはアスペクト比100以上（特に200以上）であることが好ましい。上記アスペクト比が50未満では、ガスバリア性の発現が不十分となる。一方アスペクト比が5000を越える無機層状化合物を得ることは技術的に難しく、またコストないし経済的にも高価なものとなる。製造容易性の点からは、このアスペクト比は2000以下（さらには1500以下）であることが好ましい。ガスバリア性および製造容易性のバランスの点からは、このアスペクト比は200~3000の範囲であることが更に好ましい。フィルムないし成型品とした際の製膜性ないし成形性の点からは、後述する方法により測定した「粒径」が $5\mu\text{m}$ 以下であることが好ましい。この粒径が $5\mu\text{m}$ を越えると、樹脂組成物としての製膜性ないし成形性が低下する傾向が生じる。樹脂組成物の透明性の点からは、この粒径は $3\mu\text{m}$ 以下であることが好ましい。本発明のフィルムないし成型品を透明性が重視される用途（例えば食品用途）に用いる場合には、この粒径は $1\mu\text{m}$ 以下であることが、特に好ましい。また、この透明性は、波長500nmの全光線透過率で、80%以上（さらには85%以上）の程度であることが好ましい。このような透明性は、例えば、市販の分光光度計（日立製作所製、自記分光光度計330型）で好適に測定する事が可能である。無機層状化合物の具体例としては、グラファイト、リン酸塩系誘導体型化合物（リン酸ジルコニウム系化合物）、カルコゲン化合物〔IV族（Ti, Zr, Hf）、V族（V, Nb, Ta）およびVI族（Mo, W）のジカルコゲン化合物であり、式 MX_2 で表わされる。ここで、Xはカルコゲン（S, Se, Te）を示す。〕、粘土系鉱物などをあげることができる。本発明に用いられる無機層状化合物として、粒径が $5\mu\text{m}$ 以下、アスペクト比が50以上5000以下であるものならば特に限定されない。もちろん生態系で毒性の殆どないことが必要である。粒径が $5\mu\text{m}$ より大であれば製膜性が不良となり好ましくない。また、粒径が $3\mu\text{m}$ 以下であれば透明性がより良好になり、さらに粒径が $1\mu\text{m}$ 以下であれば透明性の重視される用途にはより好ましい。アスペクト比が50未満であればガスバリア性の発現が十分でなく、5000より大

きいものは技術的に難しく、経済的にも高価なものとなる。またアスペクト比が200~3000の範囲がより好ましい。無機層状化合物の例として、リン酸塩系誘導体型化合物（リン酸ジルコニウム系化合物）、粘土系鉱物などをあげることができる。

【0015】大きなアスペクト比を有する無機層状化合物としては、溶媒に膨潤・へき開する無機層状化合物が好ましく用いられる。本発明に用いる無機層状化合物の溶媒への「膨潤・へき開」性の程度は、以下の「膨潤・へき開」試験により評価することができる。該無機層状化合物の膨潤性は、下記膨潤性試験において約5以上（さらには約20以上）の程度であることが好ましい。一方、該無機層状化合物のへき開性は、下記へき開性試験において約5以上（さらには約20以上）の程度であることが好ましい。これらの場合、溶媒としては、無機層状化合物の密度より小さい密度を有する溶媒を用いる。無機層状化合物が天然の膨潤性粘土鉱物である場合、該溶媒としては、水を用いることが好ましい。〈膨潤性試験〉

無機層状化合物2gを溶媒100mLにゆっくり加える（100mLメスシリンダーを容器とする）。ふりまぜ、静置後、23℃、24時間後の無機層状化合物分散層と上澄みとの界面の目盛りから前者（無機層状化合物分散層）の体積を読む。この数値が大きいほど膨潤性が高い。〈へき開性試験〉

無機層状化合物30gを溶媒1500mLにゆっくり加え、分散機（浅田鉄工（株）製、デスパーMH-L、羽根径52mm、回転数3100rpm、容器容量3L、底面一羽根間の距離28mm）にて周速8.5m/secで90分間分散した後（23℃）、分散液100mLをとり100mLメスシリンダーにいれ60分静置後、上澄みとの界面の目盛りから無機層状化合物分散層の体積を読む。この数値が大きいほどへき開性が高い。溶媒に膨潤・へき開する無機層状化合物としては、溶媒に膨潤・へき開性を有する粘土鉱物が好ましく使用可能である。粘土系鉱物は、一般に、シリカの四面体層の上部に、アルミニウムやマグネシウム等を中心金属にした8面体層を有する2層構造よりなるタイプと、シリカの4面体層が、アルミニウムやマグネシウム等を中心金属にした8面体層を両側から挟んだ3層構造よりなるタイプに分類される。前者としてはカオリナイト族、アンチゴライト族等を挙げることができ、後者としては層間カチオンの数によってスメクタイト族、バーミキュライト族、マイカ族等を挙げることができる。具体的には、カオリナイト、ディッカイト、ナクライト、ハロイサイト、アンチゴライト、クリソタイル、パイロフィライト、モンモリロナイト、ヘクトライト、テトラシリックマイカ、ナトリウムテニオライト、白雲母、マーガライト、タルク、バーミキュライト、金雲母、ザンソフィライト、緑泥石等をあげることができる。

【0016】樹脂組成物中での真の粒径測定はきわめて困難であるので、本発明で用いられる無機層状化合物の粒径は、溶媒中、動的光散乱法により求めた値である。動的光散乱法で用いた溶媒と同種の溶媒で十分に膨潤させて樹脂に複合させる場合、樹脂中での無機層状化合物の粒径は、溶媒中の粒径に近いと考えることができる。

【0017】本発明で用いられる無機層状化合物のアスペクト比（Z）とは、 $Z = L/a$ なる関係で示される。

〔Lは、溶媒中、動的光散乱法により求めた粒径であり、aは、無機層状化合物の単位厚みである（単位厚みaは、粉末X線回折法などによって無機層状化合物単独の測定で決められる値である。）〕。但し、 $Z = L/a$ に於いて、組成物の粉末X線回折から得られた面間隔dが存在し、 $a < d$ なる関係を満たす。ここで、 $d - a$ の値が組成物中の樹脂1本鎖の幅より大であることが必要である。Zは、樹脂組成物中の無機層状化合物の真のアスペクト比とは必ずしもいえないが、下記の理由から、かなり妥当性のあるものである。

【0018】樹脂組成物中の無機層状化合物のアスペクト比は直接測定がきわめて困難である。組成物の粉末X線回折法で得られた面間隔d、と無機層状化合物単独の粉末X線回折測定で決められる単位厚みaの間に $a < d$ なる関係があり、 $d - a$ の値が組成物中の樹脂1本鎖の幅以上であれば、樹脂組成物中において、無機層状化合物の層間に樹脂が挿入されていることになり、よって無機層状化合物の厚みは単位厚みaとなっていることは明らかである。また、樹脂組成物中での真の粒径測定はきわめて困難であるが、動的光散乱法で用いた溶媒と同種の溶媒で十分に膨潤させて樹脂に複合させる場合を考えれば、樹脂中での無機層状化合物の粒径は溶媒中のそれとかなり近いと考えることができる（但し、動的光散乱法で求められる粒径Lは、無機層状化合物の長径 L_{max} を越えることはないと考えられるから、真のアスペクト比 L_{max}/a は、本発明でのアスペクト比の定義Zを下回することは理論的には有り得ない。）。上記2点から、本発明のアスペクト比の定義は妥当性の比較的高いものと考えられる。本発明において、アスペクト比または粒径とは、上記で定義したアスペクト比、粒径を意味するものである。a、dの求め方についての詳細については、例えば、岩生周一ら編、粘土の事典、35頁以下および271頁以下、1985年、（株）朝倉書店を参照することができる（さらには、図4~10を参照）。また、組成物中の樹脂1本鎖の幅はシミュレーション計算等により求めることが可能であるが（例えば、岡村ら、高分子化学序論、103から110頁、1981年、化学同人を参照）、ポリビニルアルコールの場合には4~5オングストロームである（水分子では2~3オングストローム）。このように樹脂組成物の粉末X線回折において観測される回折ピーク（面間隔dに対応）の積分強度は、基準となる回折ピーク（面間隔aに対

応)の積分強度に対する相対比で2以上(さらには10以上)であることが好ましい。図4は、無機層状化合物のX線回折ピークと、該化合物の単位厚み a との関係を模式的に示すグラフである。図5は、無機層状化合物を含む樹脂組成物のX線回折ピークと、該組成物の面間隔 d との関係を模式的に示すグラフである。図6は、面間隔 d に対応するピークがハロー(ないしバックグラウンド)と重なって検出することが困難な場合における樹脂組成物のX線回折ピークと、該組成物の面間隔 d との関係を模式的に示すグラフである。この図においては、 $2\theta d$ より低角側のベースラインをのぞいた部分の面積を、面間隔 d に対応するピークとしている(θd は「単位厚み a +樹脂一本鎖の幅」に相当する回折角である)。図7は、ポリビニルアルコールPVA117H/グニピアF組成物のX線回折ピークを示すグラフおよびクニピアF(モンモリロナイト)のX線回折ピークを示すグラフである。図8は、面間隔 $d=19.62$ オングストロームの組成物のX線回折ピーク(図bのパターン)を示すグラフである。図9は、面間隔 $d=32.94$ オングストロームの組成物のX線回折ピーク(図5と図6のパターンあり)を示すグラフである。図10は、面間隔 d が44.13オングストローム以上の組成物のX線回折ピーク(図6のパターン)を示すグラフである。

【0019】本無機層状化合物を膨潤させる溶媒は、特に限定されないが、例えば天然の膨潤性粘土鉱物の場合、水、メタノール等のアルコール類、ジメチルホルムアミド、ジメチルスルホキシド、アセトン等が挙げられ、水やメタノール等のアルコール類がより好ましい。

【0020】本発明で用いられる樹脂が、高水素結合性樹脂であるときには、その耐水性(耐水環境テスト後のバリア性の意味)を改良する目的で水素結合性基用架橋剤を用いることができる。

【0021】水素結合性基用架橋剤としては特に限定されないが、例えば、チタン系カップリング剤、シラン系カップリング剤、メラミン系カップリング剤、エポキシ系カップリング剤、イソシアネート系カップリング剤、銅化合物、ジルコニア化合物などが挙げられ、より好ましくは、ジルコニア化合物が挙げられる。

【0022】ジルコニア化合物の具体例としては、例えば、オキシ塩化ジルコニウム、ヒドロキシ塩化ジルコニウム、4塩化ジルコニウム、臭化ジルコニウム等のハロゲン化ジルコニウム、硫酸ジルコニウム、塩基性硫酸ジルコニウム、硝酸ジルコニウムなどの鉱酸のジルコニウム塩、蟻酸ジルコニウム、酢酸ジルコニウム、プロピオン酸ジルコニウム、カプリル酸ジルコニウム、ステアリン酸ジルコニウムなどの有機酸のジルコニウム塩、炭酸ジルコニウムアンモニウム、硫酸ジルコニウムナトリウム、酢酸ジルコニウムアンモニウム、蔞酸ジルコニウムナトリウム、クエン酸ジルコニウムナトリウム、クエン

酸ジルコニウムアンモニウムなどのジルコニウム錯塩、などがあげられる。

【0023】水素結合性基用架橋剤の添加量は、架橋剤の架橋生成基のモル数(CN)と高水素結合性樹脂の水素結合性基のモル数(HN)の比(K)〔即ち、 $K=CN/HN$ 〕が、0.001以上10以下の範囲であれば、特に限定されないが、好ましくは、0.01以上1以下の範囲である。

【0024】無機層状化合物と樹脂よりなる組成物の配合方法は、特に限定されないが、例えば、樹脂を溶解させた液と、無機層状化合物を予め膨潤・へき開させた分散液とを混合後、溶媒を除く方法、無機層状化合物を膨潤・へき開させた分散液を樹脂に添加し、溶媒を除く方法、樹脂を溶解させた液に無機層状化合物を加え、膨潤・へき開させた分散液とし、溶媒を除く方法、また樹脂と無機層状化合物を熱混練する方法、などが挙げられる。とりわけ大きなアスペクト比を容易に得る方法として前三者が好ましく用いられる。

【0025】上述の前二者の方法において、溶媒を系から除去後、 110°C 以上 220°C 以下で熱エージングすることにより、とりわけフィルムの耐水性(耐水環境テスト後のバリア性の意味)が向上する。エージング時間に限定はないが、フィルムが少なくとも設定温度に到達する必要があり、例えば熱風乾燥機のような熱媒接触による方法の場合、1秒以上100分以下が好ましい。熱源についても特に限定はなく、熱ロール接触、熱媒接触(空気、オイルなど)、赤外線加熱、マイクロ波加熱、など種々のものが適用できる。また、ここでいう耐水性の効果は、樹脂が特に高水素結合性樹脂のとき、無機層状化合物が膨潤性をもつ粘土鉱物であるとき、著しく高い。

【0026】本発明において用いられる無機層状化合物と生分解性高水素結合性樹脂との組成比(体積比)は、特に限定はないが、無機層状化合物/生分解性高水素結合性樹脂の体積比が $5/95\sim 90/10$ の範囲であることが好ましく、また体積比が $5/95\sim 50/50$ であることがより好ましい。また、 $5/95\sim 30/70$ の範囲では膜の柔軟性がよくなり、 $7/93\sim 17/83$ の範囲では折れ曲げによるバリア性低下が小さくなり、剥離強度が強くなるなどの利点を有する。無機層状化合物の体積分率が $5/95$ より小さい場合には、バリア性能が十分でなく、 $90/10$ より大きい場合には製膜性が良好ではない。

【0027】無機層状化合物と生分解性高水素結合性樹脂より成る組成物の配合方法は、特に限定されない。生分解性高水素結合性樹脂を溶解させた液と、無機層状化合物を予め膨潤・へき開させた分散液とを混合後、溶媒を除く方法、無機層状化合物を膨潤・へき開させた分散液を生分解性高水素結合性樹脂に添加し、溶媒を除く方法、また生分解性高水素結合性樹脂と無機層状化合物を

熱混練する方法、などがある。とりわけ大きなアスペクト比を容易に得る方法として前二者が好ましく用いられる。

【0028】積層形態はフィルム、シート、容器など特に限定されない。但し、積層体の基材樹脂は、生分解性樹脂に限定される。生分解性樹脂とは、生体で合成される生体高分子（およびその化学修飾されたもの）または生分解性の合成高分子である。例えば、セルロースおよびヒドロキシメチルセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロースなどのセルロース誘導体、アミロース、アミロペクチン、プルラン、カードラン、ザンタン、キチン、キトサン、などの多糖類およびその化学修飾物、ポリ-3-ヒドロキシブチレート、3-ヒドロキシブチレート-3-ヒドロキシワレレート共重合体などの微生物産生ポリエステルや、生分解性脂肪族ポリエステル、ポリビニルアルコール、ポリエチレングリコール、など酵素分解性の合成高分子があげられる。

【0029】また、基材にこの様な組成物を積層する方法としては、特に限定されないが、塗工液を基材フィルム表面に塗布、乾燥、熱処理を行うコーティング方法が好ましい。コーティング方法としては、ダイレクトグラビア法やリバースグラビア法及びマイクログラビア法、2本ロールビートコート法、ボトムフィード3本リバースコート法等のロールコーティング法、及びドクターナイフ法やダイコート法、ディップコート法、バーコーティング法やこれらを組み合わせたコーティング法などの方法が挙げられる。

【0030】塗膜厚は、基材の種類および目的とするバリア性能により異なるが、乾燥厚みで10 μ m以下が好ましく、透明性が要求される場合1 μ m以下がより好ましい。下限については特に制限はないが、効果的な気体遮断効果を得るためには1nm以上であることが好ましい。

【0031】また、本発明の効果を損なわない範囲で、本フィルムおよび成形品には、紫外線吸収剤、着色剤、酸化防止剤等のさまざまな添加剤を混合してもよく、積層化の際の接着剤や印刷インキなどはもちろん用いてもよい。

【0032】

【発明の効果】本発明によれば、生分解性を保ったまま、非常に高いバリア性を有するフィルムおよび成形品を得ることができる。本発明は、フィルムとして、味噌、鰹節、菓子、ラーメン、ハム、ソーセージ、レトルト食品、コロッケなどの冷凍食品など食品包装用や薬品、精密材料包装などに用いられ、ボトル、トレイなどの成形品として、マヨネーズのスクイズボトル、ジュース、醤油、食用油、ソース、電子レンジ食品トレイ、ヨーグルトのカップ、などに用いられ、埋め立てゴミの低減に大きく寄与できる。

【0033】

【実施例】以下実施例により本発明を詳細に説明するが、本発明はこれに限定されるものではない。

【0034】各種物性の測定方法を以下に記す。

【生分解性テスト】底に1cm角の穴を4個あけた1000mLポリカップに培土（太平物産製くみあい太平園芸培土：窒素0.35g/リン酸1.5g/カリウム0.35g pH6.0～6.5）約500mLをいれ、膜厚約150 μ m、底面積約28.4cm²のサンプルフィルムを3枚、重ならないようにいれ、上からさらに前述の培土をかぶせ、1000mLポリカップ一杯に満たした。これを所定の場所に置き、培土が常に湿った状態を保つために水を供給（3日に1回）しながら経時させた。一ヶ月後、二ヶ月後にそれぞれサンプリングを行い、フィルムの外観および残留面積率にて劣化の度合を判定した。

場所：大阪府高槻市塚原2丁目10番1号 住友化学工業株式会社構内露地

期間：1993年6月4日～8月9日（約2ヶ月）

残留面積率：生分解性テストで残ったフィルムの底面積の割合を次式で求めた。

$$\left(\frac{\text{分解テスト後のフィルムの底面積}}{\text{分解前のフィルム底面積}} \right) \times 100$$

値が小さいほど生分解性が優れていることを示す。

外観：変化無し○、孔生成△、形状変化大×、原形ほとんどなし××

外観変化が大きいほど分解性に優れていることをしめす。

【酸素透過度】酸素透過度測定装置（OX-TRAN 10/50A、MOC CON社製）、温度31℃（調湿恒温槽21℃）で測定した（相対湿度は約61%を示した）。

【厚み測定】0.5 μ m以上はデジタル厚み計により測定した。0.5 μ m未満は重量分析法（一定面積のフィルムの重量測定値をその面積で除し、さらに組成物比重で除した。）または、本発明の組成物と基材の積層体の場合などは、元素分析法（積層体の特定無機元素分析値（組成物層由来）と無機層状化合物単独の特定元素分率の比から本発明の樹脂組成物層と基材の比を求める方法）によった。

【粒径測定】超微粒子粒度分析計（BI-90、ブルックヘブン社製）、温度25℃、水浴媒の条件で測定した。動的光散乱法による光子相関法から求めた中心径を粒径Lとした。

【アスペクト比計算】X線回折装置（XD-5A、（株）島津製作所製）を用い、無機層状化合物単独と樹脂組成物の粉末法による回折測定を行った。これにより無機層状化合物の面間隔（単位厚み）aを求め、さらに樹脂組成物の回折測定から、無機層状化合物の面間隔が広がっている部分があることを確認した。上述の方法で求めた粒径Lをもちいて、アスペクト比Zは、 $Z = L/a$ の式により決定した。

【0035】（実施例1）天然モンモリロナイト（クニピアF；クニミネ工業（株）製）をイオン交換水（ $0.7 \mu\text{S}/\text{cm}$ 以下）に2wt%となるように分散させ、これを無機層状化合物分散液（A液）とする。当該モンモリロナイトの粒径は560nm、粉末X線回折から得られるa値は1.2156nmであり、アスペクト比は461である。また、ポリビニルアルコール（PVA117H；（株）クラレ製、ケン化度：99.6%、重合度1700）をイオン交換水（ $0.7 \mu\text{S}/\text{cm}$ 以下）に2wt%となるように溶解させこれを樹脂溶液（B液）とする。A液とB液とをそれぞれの固形成分比（体積比）が無機層状化合物／樹脂＝3／7となるように混合し、これを塗工液とした。厚さ150 μm のポリ-3-ヒドロキシブチレート（バイオポール 0%HV；ICI製）のコロナ処理したものを基板フィルムとして、この基板フィルム上に組成液を塗布し、室温で乾燥させ、80℃で2時間さらに乾燥させることにより積層フィルムを得た。当該塗工層の乾燥厚みは μm であった。この積層フィルムの31℃、61%RHにおける酸素透過度は、 $0.09\text{cc}/\text{m}^2/\text{day}$ となり、ガスバリア性に優れたものであった。一方、生分解性テストの結果、分解によりできた穴が多数みられ、残存面積率も55%と分解性に優れたものであった（第1表）。

【0036】（実施例2～10）第1表に記した構成であるほかは、実施例1と同様にして、酸素透過度試験と生分解性テストを行った。結果は第1表に示したとおりガスバリア性、生分解性ともに優れたものであった。

【0037】（実施例11）水素結合性基用架橋剤として、炭酸ジルコニウムアンモニウム（第一稀元素工業（株）製 ジルコゾールAC7（酸化ジルコニウム換算で15wt%含有水溶液））をポリビニルアルコールの水酸基15モルに対してジルコニウム元素1モルの比になるようにA液B液の混合液に加えた。その他は第1表に記した構成であるほかは、実施例1と同様にして、酸素透過度試験と生分解性テストを行った。結果は第1表に示したとおりガスバリア性、生分解性ともに優れたものであった。

【0038】（実施例12）水素結合性基用架橋剤として、炭酸ジルコニウムアンモニウム（第一稀元素工業（株）製 ジルコゾールAC7（酸化ジルコニウム換算

で15wt%含有水溶液））をポリビニルアルコールの水酸基15モルに対してジルコニウム元素1モルの比になるようにA液B液の混合液に加えた。その他は第1表に記した構成であるほかは、実施例1と同様にして製膜後、膜を140℃、10分加熱処理した。酸素透過度試験と生分解性テストを行った結果、第1表に示したとおりガスバリア性、生分解性ともに優れたものであった。

【0039】（比較例1～3）無機層状化合物／樹脂からなる層を配しない以外は実施例1～3と同様にして酸素透過度試験と生分解性テストを行った。結果は第1表に示したとおりガスバリア性が著しく劣ったものであった。

【0040】（比較例4）無機層状化合物分散液（A液）を用いない以外は実施例1～3と同様にして酸素透過度試験と生分解性テストを行った。結果は第1表に示したとおりガスバリア性が劣ったものであった。

【0041】（比較例5）厚さ60 μm のポリエチレンフィルムの酸素透過度試験と生分解性テストを行った。結果は第1表に示したとおりガスバリア性、生分解性に著しく劣ったものであった。

【0042】略号

PHB：ポリ-3-ヒドロキシブチレート（ICI製：品名バイオポール）

HBHV4：3-ヒドロキシブチレート（96%）-3-ヒドロキシワレレート（4%）共重合体（ICI製：品名バイオポール）

HBHV9：3-ヒドロキシブチレート（91%）-3-ヒドロキシワレレート（9%）共重合体（ICI製：品名バイオポール）

CHI：水溶性キチンキャスト 膜

CHIT：キトサンキャスト 膜

PUR：プルランキャスト膜

LDPE：低密度ポリエチレンフィルム

F：天然モンモリロナイト（クニミネ工業：品名クニピアF）

H：ポリビニルアルコール（クラレ製：ポパール117H）

Z：炭酸ジルコニウムアンモニウム水溶液（第一稀元素工業製：ジルコゾールAC7）

【表1】

10

20

30

40

	基材層 (厚み μm)	無機物含有層 [体積比](厚 μm)	酸素透過度 (30℃, 80%RH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$	生分解性	
				残存面 積率(%)	外観
実施例1	PHB (150)	F/H[3/7](0.5)	0.1以下	55	×
実施例2	HBHV4(150)	F/H[3/7](0.5)	0.1以下	78	×
実施例3	HBHV9(150)	F/H[3/7](0.5)	0.1以下	75	×
実施例4	HBHV8(150)	F/H[4/8](0.8)	0.1以下	70	×
実施例5	HBHV4(150)	F/H[2/8](1.5)	0.1以下	69	×
実施例6	HBHV4(150)	F/H[1.5/8](2.0)	0.1以下	81	×
実施例7	HBHV4(150)	F/H[1/8](1.5)	0.1以下	75	×
実施例8	CHI(50)	F/H[2/8](1.5)	0.1以下	51	×
実施例9	CHIT(50)	F/H[1.5/8](2.0)	0.1以下	40	×
実施例10	PUR(20)	F/H[1.5/8](2.0)	0.1以下	40	×
実施例11	PHB (150)	F/H[2/8](0.5) Z	0.1以下	70	×
実施例12	PHB (150)	F/H[1.5/8](0.8) Z	0.1以下	75	×
比較例1	PHB (150)	なし	50	76	×
比較例2	HBHV4(150)	なし	80	分解	××
比較例3	HBHV8(150)	なし	80	30	×
比較例4	PHB (150)	117H(0.5)	4.0	83	×
比較例5	LDPE(60)	なし	500以上	100	○

【図面の簡単な説明】

【図1】第1図は本発明の積層フィルムの1態様例を示す概念図である。

【図2】第2図は本発明の積層フィルムの1態様例を示す概念図である。

【図3】第3図は本発明の積層フィルムの1態様例を示す概念図である。

【図4】第4図は、無機層状化合物のX線回折ピークと、該化合物の単位厚み a との関係を模式的に示すグラフである。

【図5】第5図は、無機層状化合物を含む樹脂組成物のX線回折ピークと、該組成物の面間隔 d との関係を模式的に示すグラフである。

【図6】第6図は、面間隔 d に対応するピークがハロー（ないしバックグラウンド）と重なって検出することが困難な場合における樹脂組成物のX線回折ピークと、該組成物の面間隔 d との関係を模式的に示すグラフであ

る。

【図7】第7図は、ポリビニルアルコールPVA117H/クニピアF組成物のX線回折ピークを示すグラフおよびクニピアF（モンモリロナイト）のX線回折ピークを示すグラフである。

【図8】第8図は、面間隔 $d = 19.62$ オングストロームの組成物のX線回折ピーク（図5のパターン）を示すグラフである。

【図9】第9図は、面間隔 $d = 32.94$ オングストロームの組成物のX線回折ピーク（図5と図6のパターン）を示すグラフである。

【図10】第10図は、面間隔 d が 44.13 オングストローム以上の組成物のX線回折ピーク（図6のパターン）を示すグラフである。

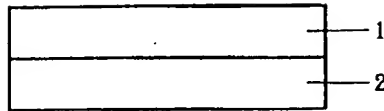
【符号の説明】

- 1 無機層状化合物を含む生分解樹脂層
- 2 生分解樹脂層

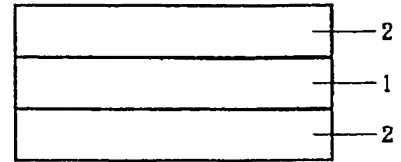
【図1】



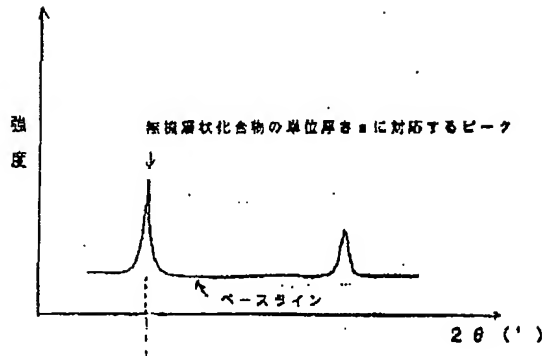
【図2】



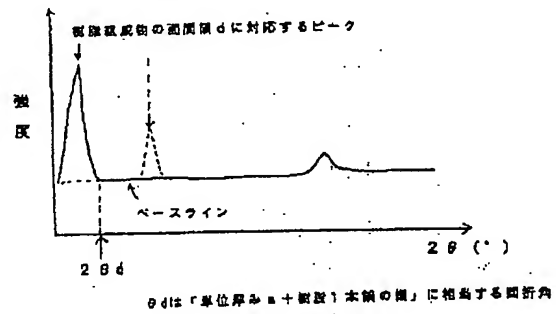
【図3】



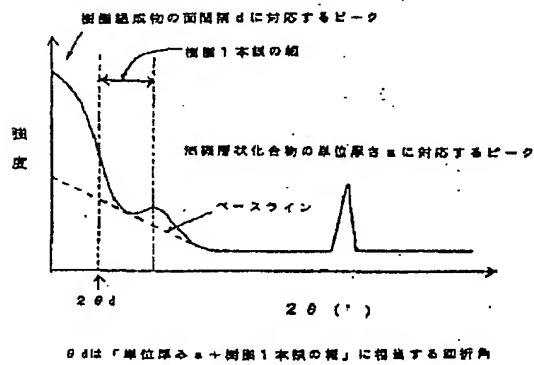
【図4】



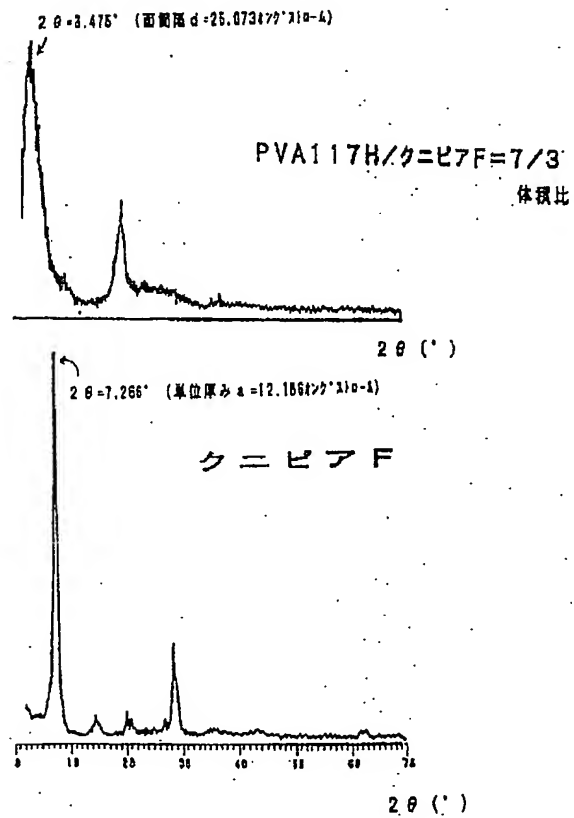
【図5】



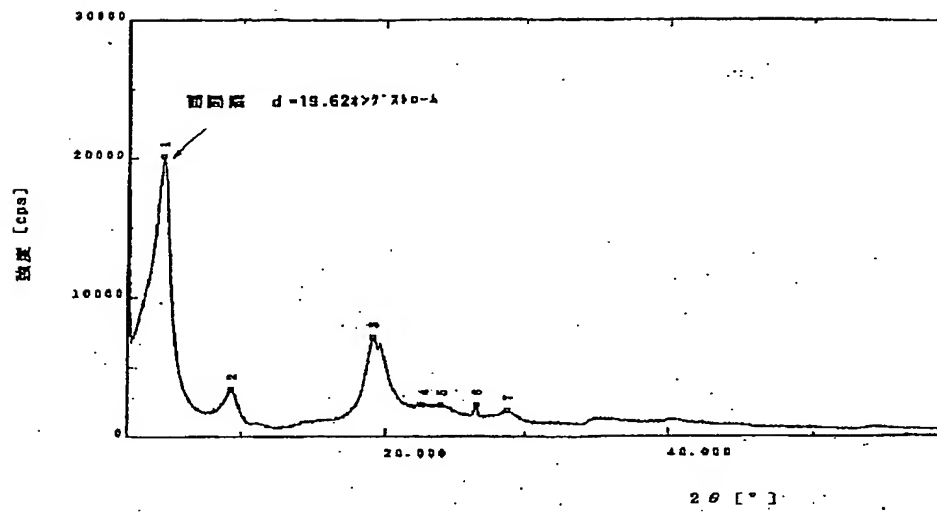
【図6】



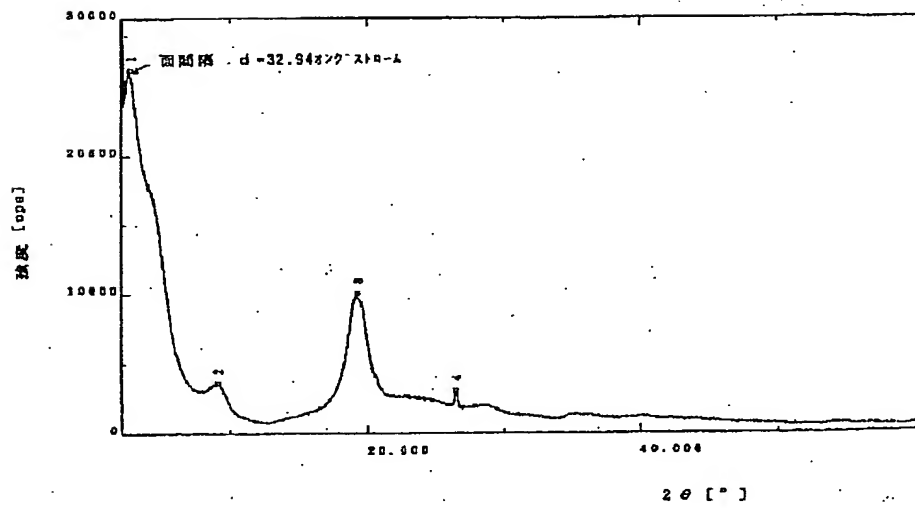
【図7】



【図8】



【図9】





US005766751A

United States Patent [19]

Kotani et al.

[11] Patent Number: **5,766,751**[45] Date of Patent: **Jun. 16, 1998**

[54] **LAMINATE, LAMINATE FILM AND SHAPED ARTICLE COMPRISING INORGANIC LAMINAR COMPOUND**

[75] Inventors: **Kozo Kotani, Toyonaka; Toshio Kawakita, Funabashi; Taiichi Sakaya; Toshiya Kuroda, both of Takatsuki, all of Japan**

[73] Assignee: **Sumitomo Chemical Company, Ltd., Osaka, Japan**

[21] Appl. No.: **522,425**

[22] PCT Filed: **Jan. 24, 1995**

[86] PCT No.: **PCT/JP95/00073**

§ 371 Date: **Sep. 22, 1995**

§ 102(e) Date: **Sep. 22, 1995**

[87] PCT Pub. No.: **WO95/19887**

PCT Pub. Date: **Jul. 27, 1995**

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Jan. 26, 1994	[JP]	Japan	6-007027
Jan. 26, 1994	[JP]	Japan	6-007029

[51] Int. Cl.⁶ **B32B 5/16**

[52] U.S. Cl. **428/323; 428/325; 428/328; 428/331; 428/410; 428/913**

[58] Field of Search **428/323, 331, 428/325, 480, 910, 913, 328**

[56] **References Cited**

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Primary Examiner—H. Thi Le

Attorney, Agent, or Firm—Cushman Darby & Cushman IP Group of Pillsbury Madison & Sutro, LLP

[57] **ABSTRACT**

A laminate, laminate film or shaped article, which includes: a layer of a substance having a gas barrier property; and at least one layer or portion (1) disposed thereon comprising a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000. As the gas barrier substance, a metal or oxide, ethylene-vinyl alcohol copolymer, or polyvinylidene chloride may preferably be used.

Such a laminate, laminate film or shaped article may exhibit a good gas barrier property which is much higher than that of a conventional plastic material.

27 Claims, 10 Drawing Sheets

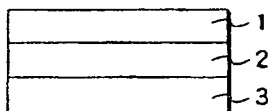


Fig. 1

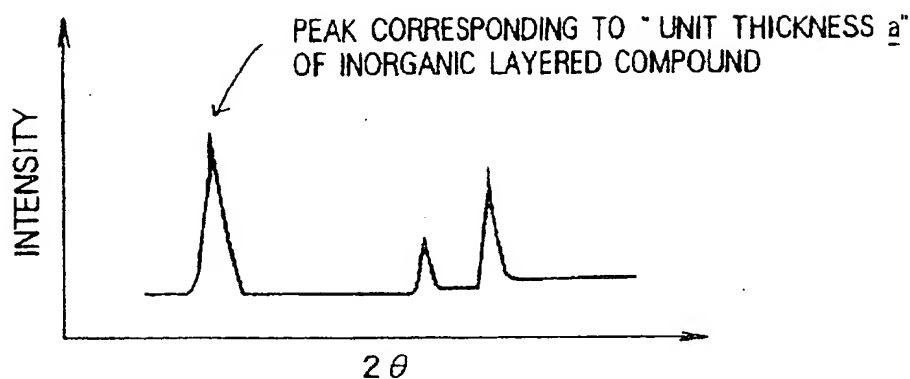
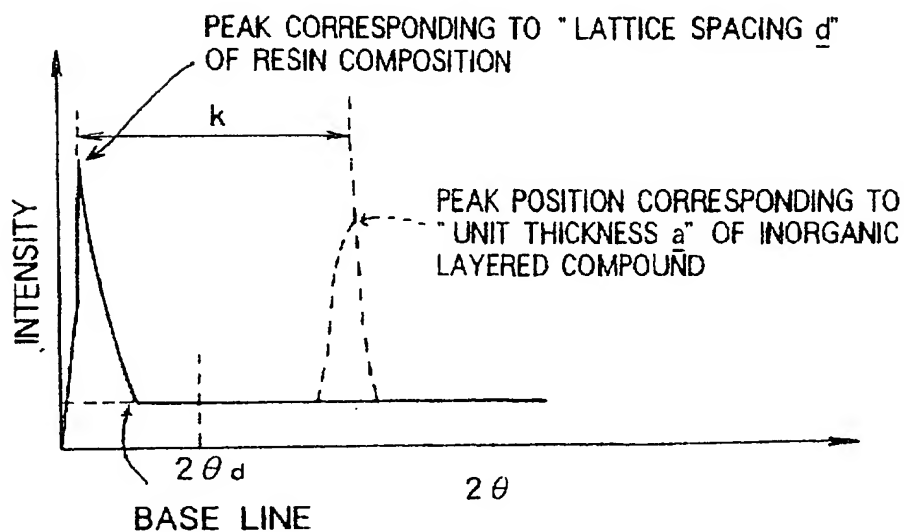


Fig. 2



" k " (IN TERMS OF LENGTH) IS NOT SMALLER THAN WIDTH OF ONE RESIN CHAIN

θ_d → ANGLE OF DIFFRACTION CORRESPONDING TO "UNIT THICKNESS \underline{a} +WIDTH OF ONE RESIN CHAIN"

Fig. 3

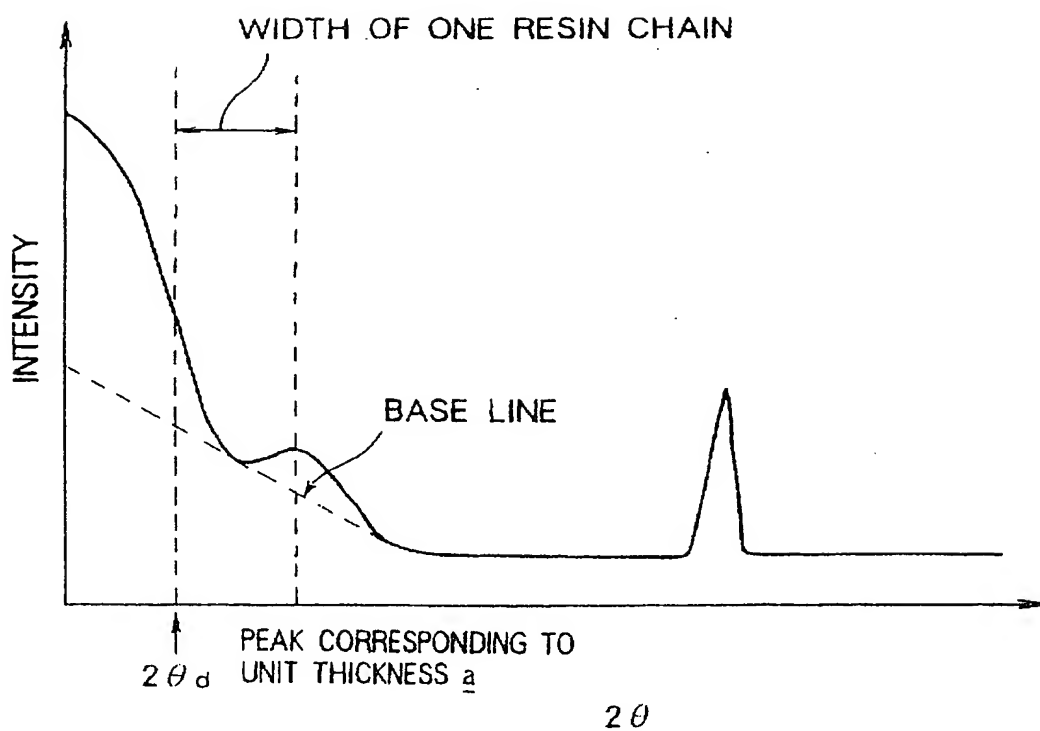


Fig. 4

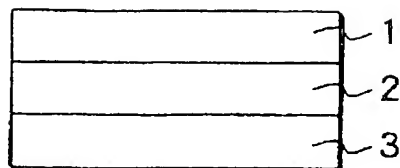


Fig. 5

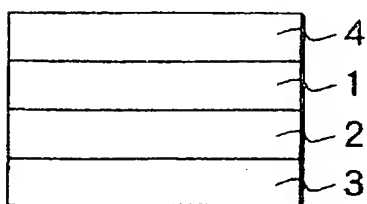


Fig. 6

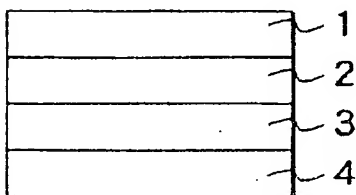


Fig. 7

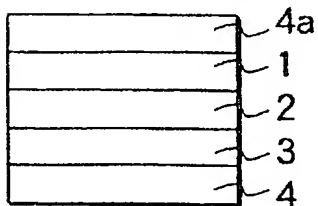


Fig. 8

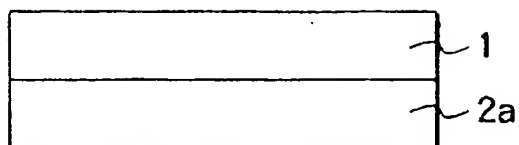


Fig. 9

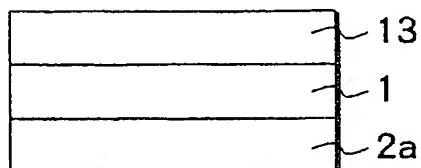


Fig. 10

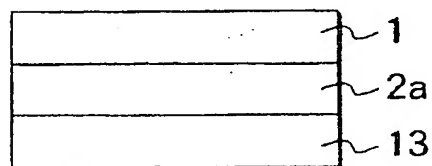


Fig. 11

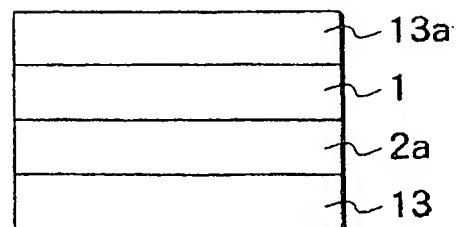


Fig. 13

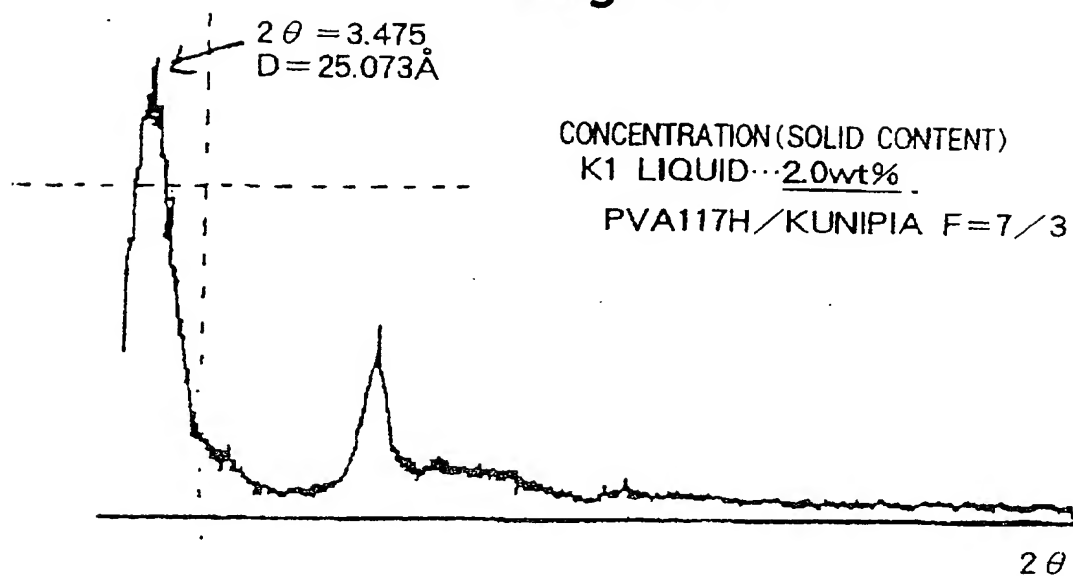


Fig. 12

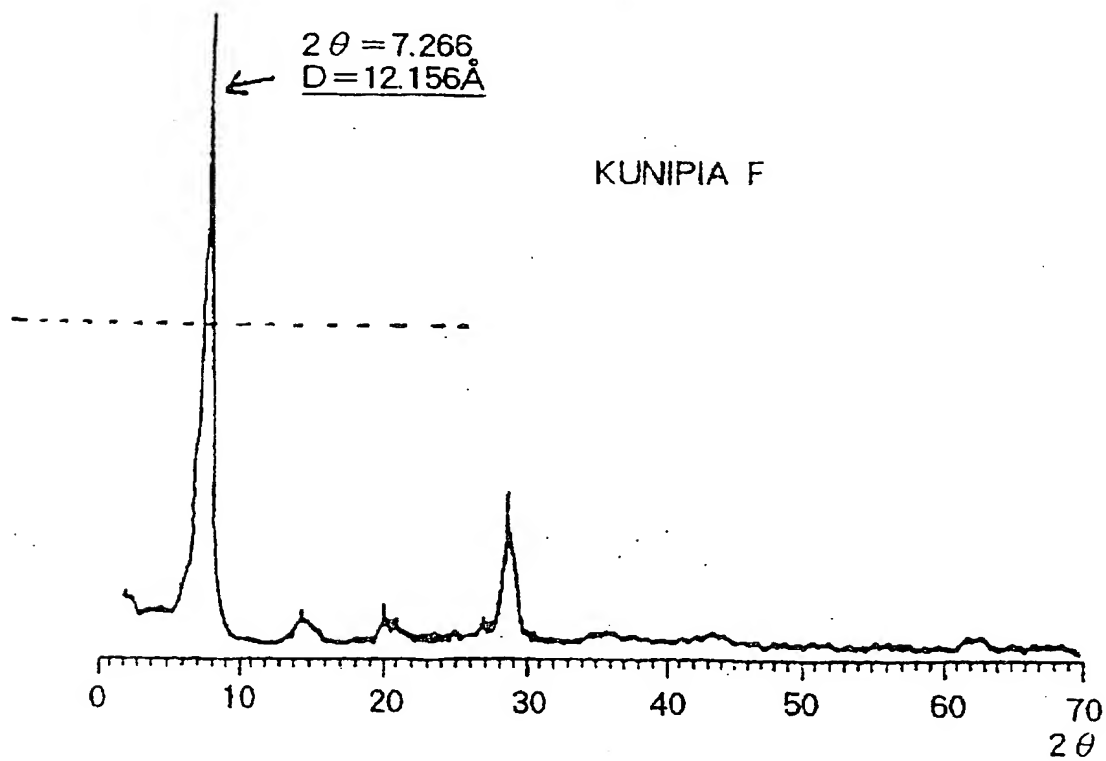


Fig. 14

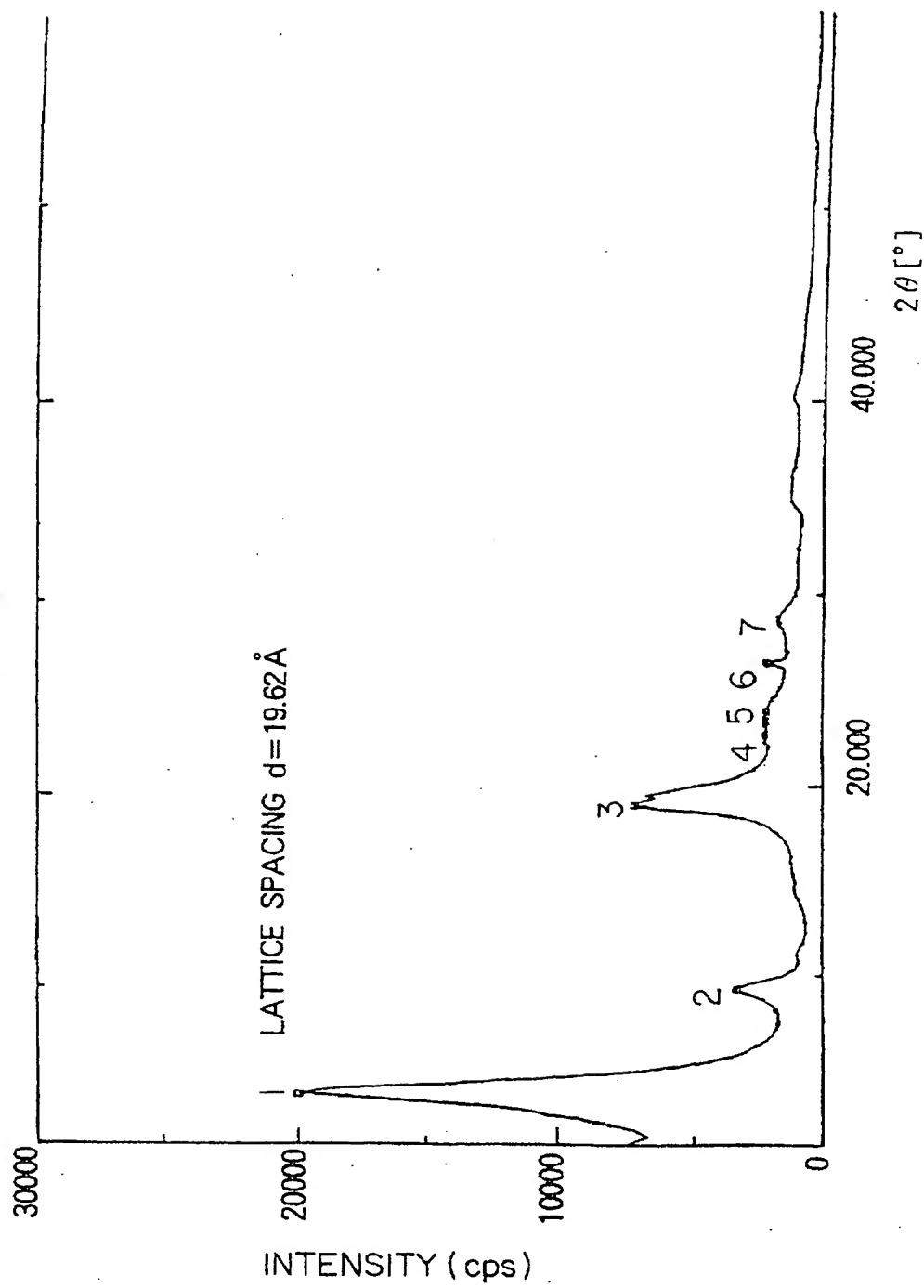


Fig. 15

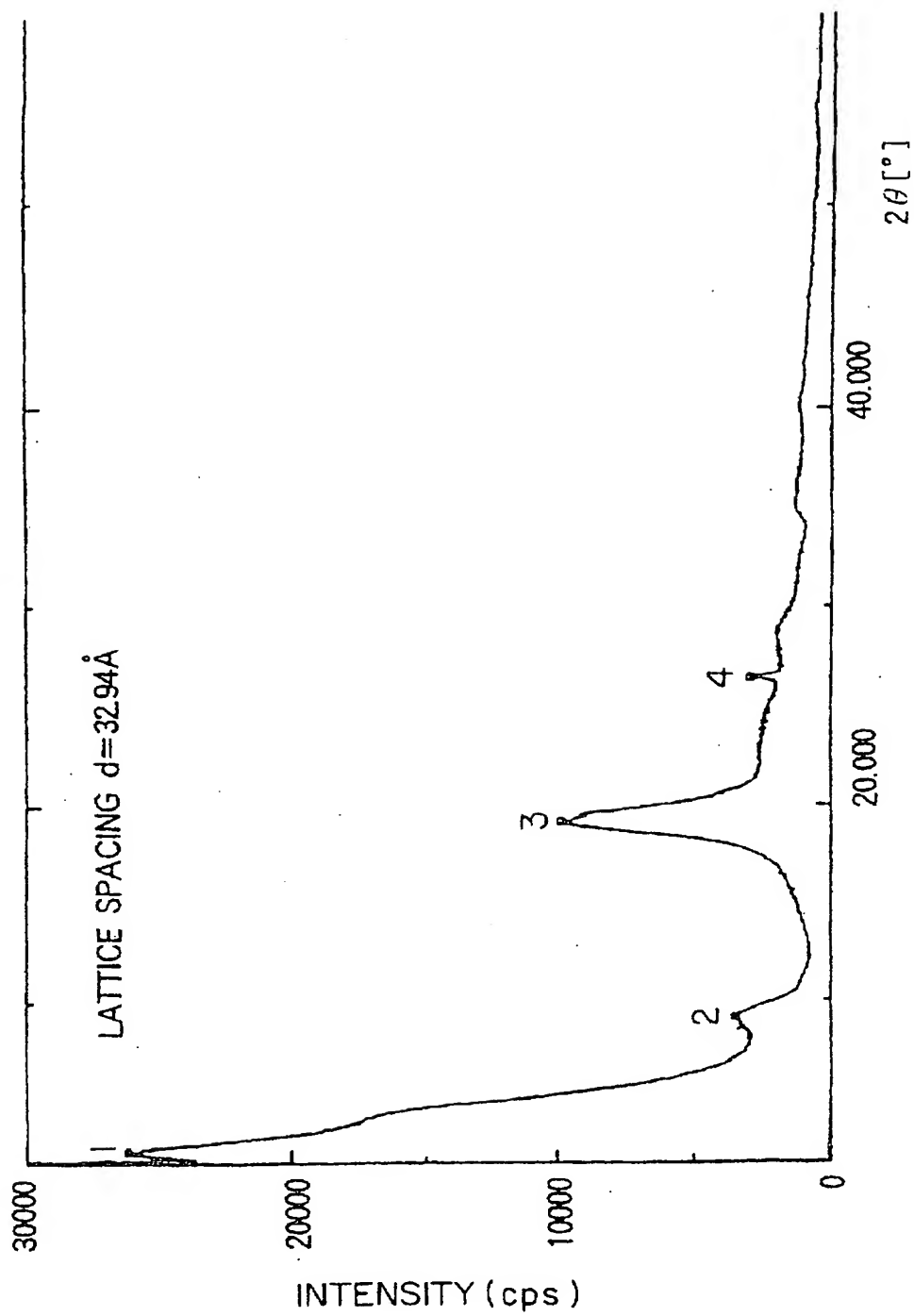


Fig. 16

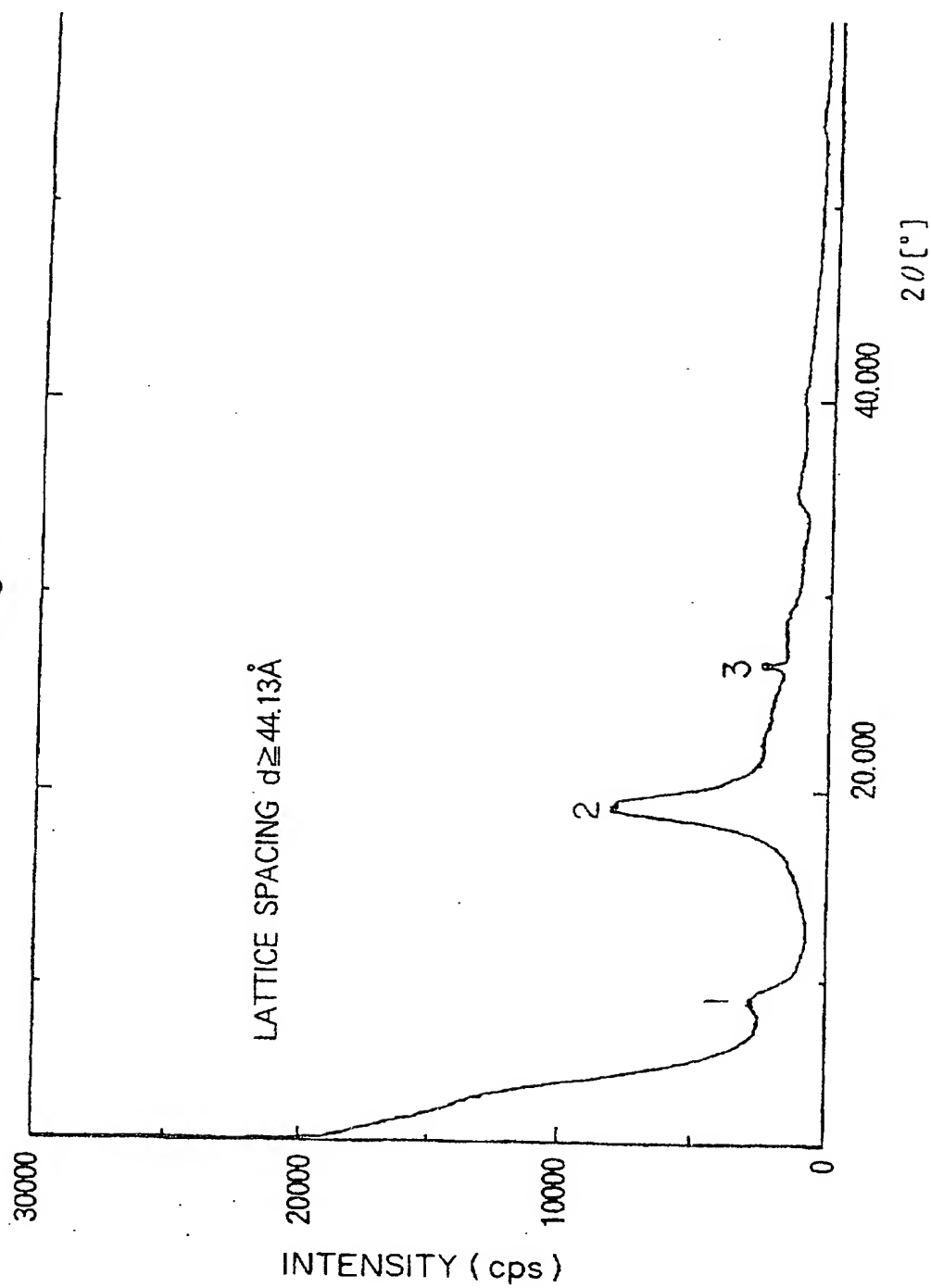


Fig. 17

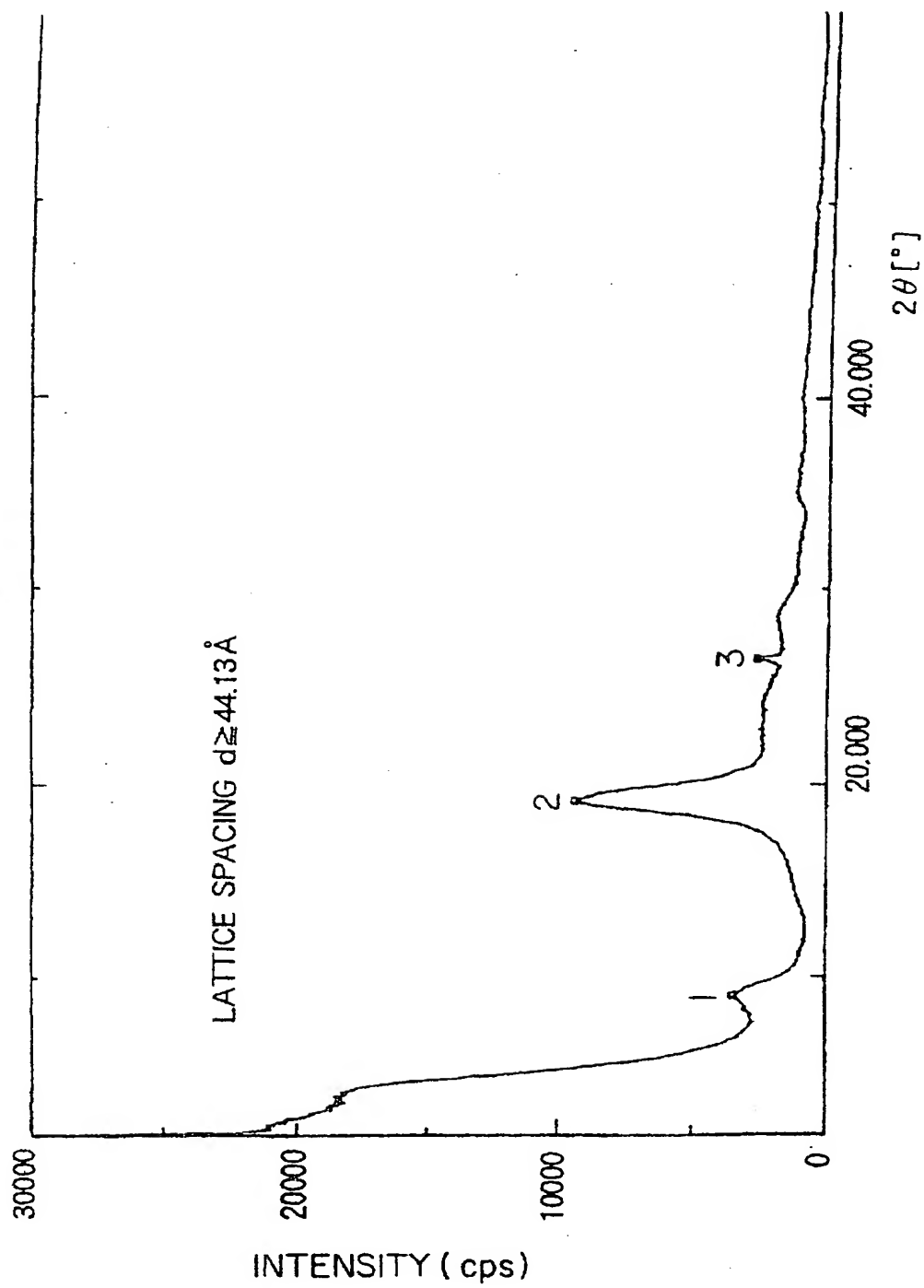
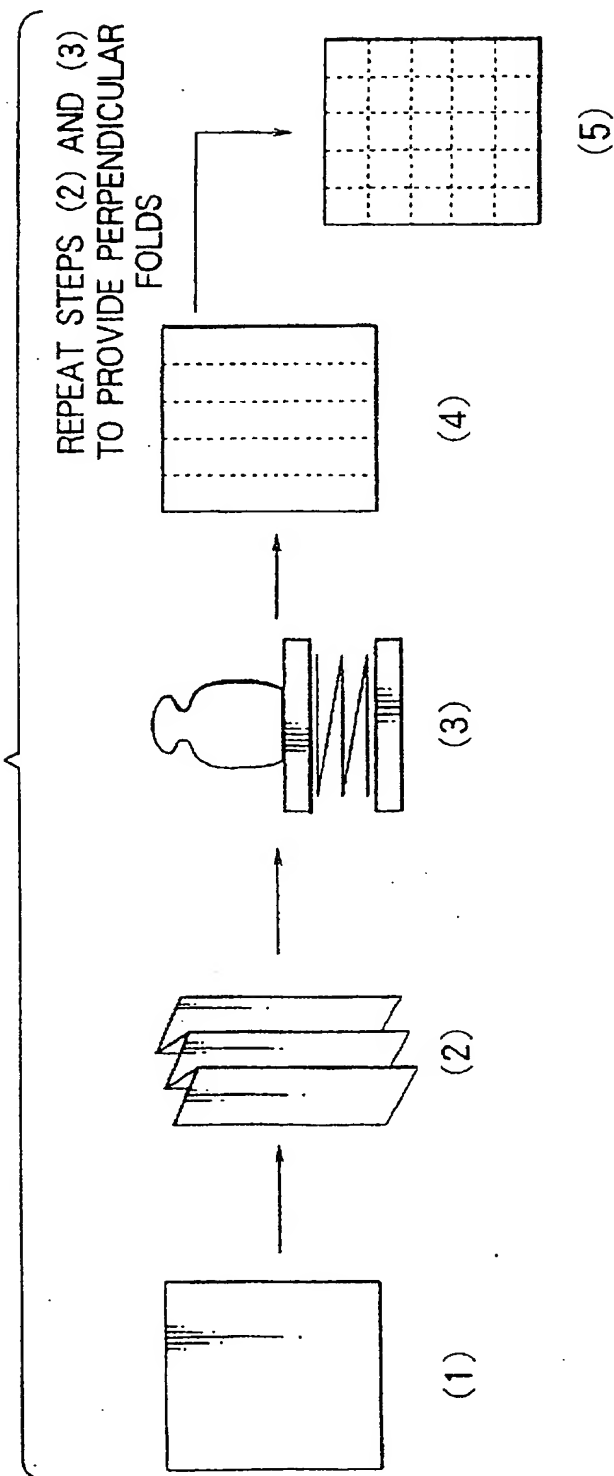


Fig. 18



LAMINATE, LAMINATE FILM AND SHAPED ARTICLE COMPRISING INORGANIC LAMINAR COMPOUND

This application claims benefit of International application PCT/JP/00073, filed Jan. 24, 1995.

TECHNICAL FIELD

The present invention relates to a laminate or laminate film which comprises at least one layer (or at least a portion) comprising a resin composition having an excellent gas barrier property, and a shaped (or molded) article comprising a portion of such a resin composition.

BACKGROUND ART

A film having a gas barrier property (gas barrier film) as a kind of functional film has widely been put to practical use in the fields of food, medicine, agricultural chemicals, cosmetics, etc., wherein contents are stored or protected while the "quality" of the contents is liable to cause a problem. One of such important usage includes a field of "packaging".

Packaging, i.e., making or putting an object into a package or wrap, or the material therefor is desired to have a wide variety of functions. For example, such functions of packaging may include: mechanical protective property, safety, sanitary property, workability, adaptability to goods (transparency, printability, heat sealing property), utility, profitability, etc. Among these functions, various "gas barrier property", as one of the factors in the above-mentioned storability or protective property, is an important property for affecting the storability of the above contents such as food. Along with recent diversification in the form of goods distribution or in packaging technique, intensification of additive control, change in taste, etc., the importance of the gas barrier property has been increased more and more. On the other hand, the gas barrier property has heretofore been a serious weak point of ordinary plastic materials.

Factors which can deteriorate a food include oxygen, light, heat and/or moisture. Among these factors, oxygen has been considered to be a substance causing such deterioration. A material having a gas barrier property (gas barrier material) is a material which has a main function of effectively intercepting oxygen. Such a gas barrier material exhibits the function of intercepting oxygen, and simultaneously exhibits a function which is essential for various measures for controlling the deterioration of food (such as gas charging and vacuum packaging). The gas barrier material has been utilized very effectively in many fields such as food packaging inclusive of confectionery bags, bags for dried bonito, pouches for retorted foods, containers for carbonated drinks, etc., or packaging for cosmetics, agricultural chemicals, and medical use, on the basis of its barrier function to various species of gases such as oxygen, organic solvent vapors, aromas; or its function of preventing corrosion, odor, sublimation, etc., based on the barrier function thereof.

Among films comprising a thermoplastic resin, those films comprising oriented polypropylene, polyester, polyamide, etc., particularly have excellent mechanical property, heat resistance, transparency, etc., and therefore these films are widely used as a packaging material. However, in a case where a film comprising such a material is used for food packaging, since the barrier property thereof to a gas such as oxygen is insufficient, the food as the contents in the package is liable to be deteriorated due to

degradation based on oxidation, or the function of aerobic bacteria, etc. Furthermore, in such a case, an aroma component of the food permeates the package to be diffused to the outside of the package. As a result, there tends to occur various problems such that the flavor of the food is lost, or the content is wetted with outside moisture due to the penetration of such moisture and the taste thereof becomes worse. Accordingly, when a film of the above-mentioned material such as polypropylene is used for food packaging, it is usual to adopt a method wherein another film (or layer) having an excellent gas barrier property is laminated onto the film of the above-mentioned material.

As a method of imparting a gas barrier property or increasing the gas barrier property of a resin, there has been known a method wherein an inorganic material in a flat shape is dispersed in a resin. For example, Japanese Laid-Open Patent Application (KOKAI) No. 148532/1987 (i.e., Sho 62-148532) describes a process for producing a film having a gas barrier property wherein a coating liquid composition comprising 100 wt. parts of a polyurethane resin solution (concentration: 30%) using 1,6-hexanepolycarbonatediol, 25 wt. parts of mica fine powder, and 60 wt. parts of dimethylformamide is applied onto a base material having a releasability, and then is dried and peeled from the base material.

In addition, Japanese Laid-Open Patent Application No. 043554/1989 (i.e., Sho 64-043554) describes a process for producing a film wherein mica having an average length of 7 μ m and an aspect ratio of 140 is added into an aqueous methanol solution of an ethylene-vinyl alcohol copolymer, and the resultant mixture is poured into cold water, and then subjected to filtration and drying to provide pellets, which are then formed into a film.

Furthermore, Japanese Laid-Open Patent Application No. 93542/1991 (i.e., Hei 3-93542) describes a process for producing a coated plastic film wherein a coating composition comprising a silyl group-containing modified polyvinyl alcohol and synthetic hectorite in a wt. ratio of 50:50, is applied onto a biaxially oriented polyethylene terephthalate (OPET), and then subjected to drying and heat treatment (130 to 150° C.).

However, such films provided by the above-mentioned conventional technique still do not have a sufficient gas barrier property, and is not a satisfactory film having a gas barrier property suitable for practical use.

As one of the important measures for imparting a gas barrier property, there has heretofore been known a method wherein a thin film is formed on at least one side of the surfaces of another film comprising a thermoplastic resin by use of a metal such as aluminum, or an oxide such as silica and alumina through vacuum vapor deposition, etc., so as to impart a barrier property to the resin film. However, during the formation of such a thin film, pin holes are liable to be formed and performances thereof tend to be considerably decreased on the basis of deformation of the film due to insufficient flexibility or mechanical strength of the thin film. As a result, such a process hardly imparts a satisfactory gas barrier property to the film.

An object of the present invention is to provide a laminate, a laminate film or a shaped article which has solved the above-mentioned problems.

A more specific object of the present invention is to provide a laminate, a laminate film or a shaped article having a gas barrier property at a good level.

DISCLOSURE OF INVENTION

As a result of earnest study, the present inventors have found that a laminate, a laminate film or a shaped article

having an excellent gas barrier property has been provided by constituting a laminate, a laminate film or a shaped article while a layer comprising a substance having a gas barrier property is further combined with a layer (or portion) of a resin composition comprising a resin and an inorganic laminar compound dispersed therein and having a specific aspect ratio.

The laminate according to the present invention is based on the above discovery and comprises: a layer comprising a substance having a gas barrier property; and

at least one layer which is disposed on the gas barrier substance layer and comprises a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000.

The present invention also provides a laminate having a shape in the form of a laminate film.

The present invention further provides a laminate film comprising: a base material; and

at least one laminate disposed thereon, which comprises a layer comprising a substance having a gas barrier property; and a layer disposed on the gas barrier substance layer and comprising a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000.

The present invention further provides a shaped article, which comprises, at least a portion thereof, a laminate portion comprising: a layer comprising a substance having a gas barrier property; and a layer disposed on the gas barrier substance layer and comprising a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph schematically showing a relationship between an X-ray diffraction peak of an inorganic laminar compound and a "unit thickness a " of the compound.

FIG. 2 is a graph schematically showing a relationship between an X-ray diffraction peak of a resin composition containing an inorganic laminar compound and a "lattice spacing (or distance between lattice planes) d " of the compound.

FIG. 3 is a graph schematically showing a relationship between an X-ray diffraction peak of a resin composition and a "lattice spacing d " of the composition, in a case where the peak corresponding to the lattice spacing d is superposed on halo (or background) and is difficult to be detected. In this Figure, the area obtained by subtracting a "base line" portion from the peak area in the lower angle side below $2\theta_d$ is treated as the peak corresponding to the "lattice spacing d ".

FIG. 4 is a schematic sectional view showing an embodiment of the laminate film structure according to the present invention, which comprises a resin film 3, a layer 2 disposed on the resin film 3 and comprising a substance having a gas barrier property, and a layer 1 containing an inorganic laminar compound disposed on the layer 2 of the gas barrier substance.

FIG. 5 is a schematic sectional view showing another embodiment of the laminate film structure according to the present invention, which further comprises a "base material 4 for laminating" disposed on the inorganic laminar compound-containing layer 1 as shown in the above FIG. 4 embodiment.

FIG. 6 is a schematic sectional view showing a further embodiment of the laminate film structure according to the present invention, which further comprises a "base material

4 for laminating" disposed on the resin film 3 side as shown in the above FIG. 4 embodiment.

FIG. 7 is a schematic sectional view showing a further embodiment of the laminate film structure according to the present invention, which further comprises base materials 4 and 4a for laminating, respectively disposed on the inorganic laminar compound-containing layer 1 side and on the resin film 3 side as shown in the above FIG. 4 embodiment.

FIG. 8 is a schematic sectional view showing an embodiment of the laminate film structure according to the present invention, which comprises a layer 2a comprising a gas barrier substance having a film forming property, and a (resin composition) layer 1 containing an inorganic laminar compound disposed on the layer 2a of the gas barrier substance.

FIG. 9 is a schematic sectional view showing another embodiment of the laminate film structure according to the present invention, which further comprises a "base material 13 for laminating" disposed on the inorganic laminar compound-containing layer 1 as shown in the above FIG. 8 embodiment.

FIG. 10 is a schematic sectional view showing a further embodiment of the laminate film structure according to the present invention, which further comprises a "base material 13 for laminating" disposed on the side of the layer 2a of the gas barrier substance as shown in the above FIG. 8 embodiment.

FIG. 11 is a schematic sectional view showing a further embodiment of the laminate film structure according to the present invention, which further comprises base materials 13 and 13a for laminating, respectively disposed on the inorganic laminar compound-containing layer 1 side and on the side of the layer 2a of the gas barrier substance as shown in the above FIG. 8 embodiment.

FIG. 12 is a graph showing X-ray diffraction peaks of composition comprising a polyvinyl alcohol PVA-117H and "Kunipia F" used in Examples.

FIG. 13 is a graph showing X-ray diffraction peaks of "Kunipia F" (montmorillonite) used in Examples.

FIG. 14 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d=19.62$ angstrom (pattern of the above FIG. 2).

FIG. 15 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d=32.94$ angstrom (pattern having the above patterns of FIGS. 2 and 3).

FIG. 16 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d \geq 44.13$ angstrom (pattern of the above FIG. 3).

FIG. 17 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d \geq 44.13$ angstrom (pattern of the above FIG. 3).

FIG. 18 is a schematic view for illustrating a folding method used in a "folding test" as described hereinafter.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinbelow, the present invention will be described in detail with reference to the accompanying drawings, as desired.

The "inorganic laminar compound" to be used in the present invention refers to an inorganic compound wherein unit crystal layers are mutually stacked to form a layer structure. In other words, "layered compound" refers to a compound or substance having a layer structure. The "layer

structure" is a structure wherein planes, each of which comprises atoms strongly bonded to each other on the basis of covalent bonds, etc., so as to form close packing, are stacked substantially parallel on the basis of weak bonding power such as Van der Waals force.

The "inorganic laminar compound" usable in the present invention is not particularly limited, as long as the "aspect ratio" thereof measured by a method described hereinafter is not less than 50 and not more than 5000. In view of the gas barrier property, the aspect ratio may preferably be not less than 100 (particularly, not less than 200).

When the above aspect ratio is less than 50, the exhibition of the gas barrier property becomes insufficient. On the other hand, is technically difficult to obtain an inorganic laminar compound having an aspect ratio exceeding 5000, and further such a compound is costly or expensive from an economic viewpoint. In view of easiness in production of an inorganic laminar compound, the aspect ratio may preferably be not more than 2000 (more preferably, not more than 1500). In view of the balance between the gas barrier property and easiness in production, the aspect ratio may preferably be in the range of 200-3000.

In view of the film forming property or formability in the form of a film or shaped article, the "particle size" measured by a method therefor described hereinafter may preferably be not more than 5 μm . When the particle size exceeds 5 μm , the film forming property or formability of a resin composition tends to be decreased. In view of the transparency of a resin composition, the particle size may more preferably be not more than 3 μm . In a case where the resin composition according to the present invention is used for a purpose (e.g., purpose of food packaging) wherein the transparency is important, the particle size may particularly preferably be not more than 1 μm .

Specific examples of the inorganic laminar compound may include: graphite, phosphoric acid salt-type derivative compounds (such as zirconium phosphate-type compound), chalcogen-type compounds, clay-type minerals, etc. The "chalcogen-type compound" used herein refers to a di-chalcogen type compound which comprises an element of Group IV (Ti, Zr, Hf), Group V (V, Nb, Ta), and/or Group VI (Mo, W), and represented by a formula of MX_2 , wherein M denotes an element as described above, and X denotes a chalcogen (S, Se, Te).

In view of easiness in the provision of a large aspect ratio, it is preferred to use an inorganic laminar compound having a property such that it is swollen or cleft in a solvent.

The degree of the "swelling or cleavage" of the inorganic laminar compound to be used in the present invention in a solvent may be evaluated by the following "swelling or cleavage" test. The inorganic laminar compound may preferably have a swelling property of not less than about 5 (more preferably, not less than about 20) according to the following swelling test. On the other hand, the inorganic laminar compound may preferably have a cleavage property of not less than about 5 (more preferably, not less than about 20) according to the following cleavage test. In these cases, a solvent having a density smaller than the density of the inorganic laminar compound is used. When the inorganic laminar compound is a natural clay mineral having a swelling property, it is preferred to use water as the above solvent.

<Swelling property test>
2 g of an inorganic laminar compound is slowly added to 100 mL of a solvent, while 100 mL-graduated cylinder is used as a container. The resultant mixture is left standing, and thereafter the volume of the former (the dispersion layer

of the inorganic laminar compound) is read from the graduation corresponding to the interface between the dispersion layer of the inorganic laminar compound and the supernatant after 24 hours at 23° C. When the resultant value is larger, the swelling property is higher.

<Cleavage property test>

30 g of an inorganic laminar compound is slowly added to 1500 mL of a solvent, and is dispersed by means of a dispersion machine (mfd. by Asada Tekko K.K., Despa MH-L, vane diameter=52 mm, rotating speed=3100 rpm, container capacity=3 L, distance between the bottom face and the vane=28 mm) for 90 minutes at a peripheral speed of 8.5 m/sec (23° C.). Thereafter, 100 mL of the resultant dispersion liquid is taken out and placed into a graduated cylinder, and then is left standing for 60 minutes. Then, the volume of the dispersion layer of the inorganic laminar compound is read from the graduation corresponding to the interface between the dispersion layer of the inorganic laminar compound and the supernatant.

As the inorganic laminar compound capable of being swollen or cleft in a solvent, it is particularly preferred to use a clay mineral having a swelling or cleaving property. The clay minerals may be classified into two types, i.e., one type having a two-layer structure, which comprises a silica tetrahedral layer, and an octahedral layer disposed thereon and comprising a central metal such as aluminum and magnesium; and another type having a three-layer structure, which comprises an octahedral layer comprising a central metal such as aluminum and magnesium, and a silica tetrahedral layer disposed on the both sides of the octahedral layer so as to sandwich the octahedral layer.

Specific examples of the former two-layer type may include: kaolinite series, antigorite series, etc. Specific examples of the latter three-layer type may include: smectite series, vermiculite series, mica series, etc., depending on an interlayer cation contained therein.

More specific examples of the clay mineral may include: kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetrasilic mica, sodium taeniolite, muscovite, margarite, talc, vermiculite, phlogopite, xanthophyllite, chlorite, etc.

<Particle size>

In view of difficulty, etc., in measuring the (true) particle size in a resin composition, in the present invention, a value (L) which may be determined in a solvent by a dynamic light scattering method (photon correlation spectroscopy) as described hereinafter is used as the "particle size" of the inorganic laminar compound. The "dynamic light scattering method" used herein is a particle size-measuring method utilizing scattering phenomenon of laser light, wherein scattering light from particles conducting Brownian movement, i.e., scattering light with fluctuation depending on the moving velocity or particle size (grain size) of those particles, is detected, and an information on the particle size is obtained by calculation.

According to the present inventors' knowledge, the particle size of the inorganic laminar compound contained in a resin may be approximated by the above-mentioned "particle size in a solvent" obtained by the dynamic light scattering method. For example, in a case where an inorganic laminar compound which has sufficiently been swollen with a solvent (which is the same kind of the solvent used in the dynamic light scattering method) is combined with a resin, the particle size of the inorganic laminar compound contained in the resin may sufficiently be approximated by the "particle size in a solvent" obtained by the dynamic light scattering method.

(Aspect ratio)

In the present invention, the aspect ratio (Z) of the inorganic laminar compound is a ratio which may be determined on the basis of a relationship of $Z=L/a$. In this relationship, L is the particle size of an inorganic laminar compound determined by the dynamic light scattering method in a solvent, and a is the "unit thickness" of the inorganic laminar compound. The "unit thickness a " is a value which is determined on the basis of the measurement of the inorganic laminar compound alone, by powder X-ray diffraction method, etc., as described hereinafter. More specifically, as schematically shown in the graph of FIG. 1 wherein the abscissa denotes 2θ , and the ordinate denotes the intensity of X-ray diffraction peaks, the "unit thickness a " is a spacing obtained from the Bragg's equation ($n\lambda=2D\sin\theta$, $n=1, 2, 3, \dots$), wherein θ denotes the angle corresponding to the peak having the lowermost angle among those of the observed diffraction peaks. With respect to the details of the powder X-ray diffraction method, a book entitled "Kiki-Bunseki no Tebiki (Handbook on Instrumental Analysis) (a)", page 69, (1985), editorially supervised by Jiro SHIOKAWA, published by KAGAKU DOJIN K.K. may be referred to.

In correspondence to the above relationship of $Z=L/a$ based on the measurement of the inorganic laminar compound alone, when the resin composition according to the present invention is subjected to the powder X-ray diffraction method, the lattice spacing d of the inorganic laminar compound contained in the resin composition may usually be obtained.

More specifically, as schematically shown in the graph of FIG. 2 wherein the abscissa denotes 2θ , and the ordinate denotes the intensity of X-ray diffraction peaks, the "lattice spacing d " ($a < d$) is a spacing corresponding to the peak having the lowermost angle among the observed diffraction peaks appearing on the lower angle (larger spacing) side as compared with the position of the diffraction peak corresponding to the above-mentioned "unit thickness a ". In a case where the above peak corresponding to the "lattice spacing d " is superposed on a halo (or background) as schematically shown in the graph of FIG. 2 so that it is difficult to detect such a peak, the area of a portion obtained by subtracting the base line portion from a portion corresponding to an angle lower than $2\theta_d$ is treated as a peak corresponding to the "lattice spacing d ". The θ_d used herein is an angle of diffraction corresponding to "(unit length a)+(width of one resin chain)". With respect to the details of a method of determining the "lattice spacing d ", a book entitled "Nendo no Jiten (Encyclopedia of Clay)", page 35 et seq. and page 271 et seq., (1985), edited by Shuichi IWAO et al., published by ASAKURA SHOTEN K.K. may be referred to.

The integrated intensity of the diffraction peak (corresponding to the "lattice spacing d ") observed in the powder X-ray diffraction of a resin composition may preferably have a relative ratio of not less than 2 (more preferably, not less than 10), with respect to the integrated intensity of the diffraction peak as a standard (corresponding to the "lattice spacing a ").

In general, the difference between the above lattice spacing d and the "unit thickness a ", namely, the value of $k=(d-a)$ (when converted into "length") may be equal to, or larger than the width of one resin chain constituting the resin composition ($k=(d-a) \geq (\text{width of one resin chain})$). The "width of one resin chain" may be determined by simulation calculation, etc. (as described in, e.g., a book entitled "KOBUNSHI KAGAKU JORON (Introduction to Polymer

Chemistry)", pages 103-110 (1981), published by KAGAKU DOJIN K.K.). In the case of polyvinyl alcohol, this width is 4-5 Å (angstrom), and in the case of water molecules, this width is 2-3 Å.

It is considered that the above-mentioned aspect ratio $Z=L/a$ is not always equal to "true aspect ratio" of the inorganic laminar compound in the resin composition. However, it is reasonable to approximate the "true aspect ratio" by the aspect ratio Z , for the following reason.

Thus, it is extremely difficult to directly measure the "true aspect ratio" of the inorganic laminar compound contained in a resin composition. On the other hand, in a case where there is a relationship of $a < d$ between the lattice spacing d determined by the powder X-ray diffraction method for the resin composition, and the "unit thickness a " determined by powder X-ray diffraction method for the inorganic laminar compound alone; and the value of $(d-a)$ is not smaller than the width of one resin chain in the resin composition, it is assumed that the resin is inserted between layers of the inorganic laminar compound. Accordingly, it is sufficiently reasonable to approximate the thickness of the inorganic laminar compound in the resin composition by the above-mentioned "unit thickness a ", i.e., to approximate the "true aspect ratio" in the resin composition by the above-mentioned "aspect ratio Z " of the inorganic laminar compound alone.

As described above, it is extremely difficult to measure the true particle size in the resin composition. However, it may be considered that the particle size of the inorganic laminar compound in the resin is quite near to the particle size in a solvent, when the inorganic laminar compound, which has fully been swollen with a solvent of the same kind as that of the solvent used in the dynamic light scattering method, is combined with a resin to provide a resin composition.

However, it is hardly considered that the particle size L determined by the dynamic light scattering method exceeds the major axis length L_{max} of the inorganic laminar compound, and therefore the possibility that true aspect ratio (L_{max}/a) is smaller than the "aspect ratio Z " used in the present invention (i.e., the possibility of $L_{max}/a < Z$), is theoretically very small.

In view of the above-mentioned two points, it is considered that the definition of the aspect ratio Z used in the present invention is sufficiently reasonable. Thus, in the present specification, the "aspect ratio" or "particle size" means the "aspect ratio Z " as defined above, or "particle size L " determined by the dynamic light scattering method.

<Solvent>

In the present invention, the solvent for swelling the inorganic laminar compound is not particularly limited, as long as it is usable in the production of the resin composition. For example, when a natural clay mineral having a swelling property is used as an inorganic laminar compound, specific examples of the solvent may include: water, alcohols such as methanol; polar solvent such as dimethylformamide, dimethyl sulfoxide, and acetone; or mixtures comprising two or more species selected from these solvents. It is preferred to use water or an alcohol such as methanol having a relatively low boiling point, in view of easiness in the removal thereof after the film formation or shaping of the resin composition.

(Resin)

The "resin" constituting the resin composition together with the inorganic laminar compound in the present invention is not particularly limited, as long as it enables the stable dispersion or retention of the inorganic laminar compound.

(Highly hydrogen-bonding resin)

In the present invention, the "polyvinyl alcohol" refers to a polymer predominantly comprising a monomer unit of vinyl alcohol. Specific examples of such a "polyvinyl alcohol" may include: a polymer (exactly, a copolymer of vinyl alcohol and vinyl acetate) obtained by subjecting the acetic acid portion of a vinyl acetate polymer to hydrolysis or ester interchange (saponification), and polymers obtained by saponifying a polymer such as vinyl trifluoroacetate polymer, vinyl formate polymer, vinyl pivalate polymer, t-butyl vinyl ether polymer, and trimethylsilyl vinyl ether polymer. With respect to the details of the "polyvinyl alcohol", a book entitled "PVA no Sekai (World of PVA)"

A film or shaped article comprising the resin composition according to the present invention may preferably have a transparency, in view of advantage in a case where it is used for a purpose such as packaging. The transparency may preferably have a degree of not less than 80% (more preferably, not less than 85%) in terms of transmittance of whole light at a wavelength of 500 nm. For example, such

a transparency may preferably be measured by means of a commercially available spectrophotometer (automatic recording spectrophotometer Model-330, mfd. by Hitachi Seisakusho K.K.).

(Oxygen permeability)

The film or shaped article comprising the resin composition according to the present invention has a gas barrier property. The gas barrier property may preferably be not more than 0.5 cc/m²·day·atm, more preferably, not more than 0.2 cc/m²·day·atm (particularly preferably, not more than 0.15 cc/m²·day·atm), in terms of an oxygen permeability under the conditions of 30° C. and 60% RH (relative humidity).

(Resistance to folding)

The film or shaped article comprising the resin composition according to the present invention may preferably have a folding (or bending) resistance. The folding resistance may preferably be 20 or less, more preferably 10 or less (particularly preferably, 3 or less), in terms of an increment ratio R in oxygen permeability defined by $R = P_F/P_i$ (wherein P_F denotes the oxygen permeability after a folding test, and P_i denotes the oxygen permeability before the folding test), when the resin composition, laminate, or laminate film according to the present invention is subjected to a "folding test" as described hereinafter. At the time of the folding test, the resin composition is subjected to the folding test, after a layer comprising the resin composition and having a thickness after drying of 0.8 μm is formed on a biaxially oriented polypropylene film with a coating of polyvinylidene chloride (thickness=25 μm, trade name: Senesee KOP, mfd. by Daicel K.K.) so that the entirety thereof is formed into a laminated film-type shape.

<Folding test>

A 33 cm-wide non-oriented polypropylene film (trade name: Pyren Film-CT, mfd. by Toyobo K.K., thickness 50 μm) is dry-laminated onto an inorganic laminar compound-containing layer (resin composition layer) side of a laminate film to be examined by means of a laminating machine (trade name: Test-Coater, mfd. by Yasui Seiki co.) under a pressure of 4 kg/cm² at a speed of 6 m/min., while using a urethane-type adhesive (trade name: Yunoflex-J3, mfd. by Sanyo Kasei K.K.) in an amount of 3 g/m² (solid content). The resultant dry-laminated film is then sampled to be formed into a test piece form having a length of 12 cm and a width of 12 cm.

The test piece is subjected to "folding" in the following manner. Thus, as shown in FIG. 18, the test piece (Step 1) is folded into an accordion-like shape having an interval of 1 cm by using hands (Step 2). The resultant test piece is then sandwiched between two flat plates of acrylic resin (dimensions: 15 cm×15 cm, thickness: about 5 mm). A load of 5 kg is applied to the resultant sandwich-like product, and the sandwich-like product is left standing for 30 min. in this state (Step 3). Then, the application of the load is removed and the test piece is once spread (Step 4). Thereafter, the spread test piece is again subjected to the above "folding" process (Steps 2 to 3) except that the test piece is provided with folds perpendicular to the "first folds" which have been produced above, to be folded into an accordion-like shape having an interval of 1 cm, whereby a "test piece after folding" (Step 5) is obtained.

The thus prepared "test piece after folding" is subjected to oxygen permeability measurement in a manner as described hereinafter. When pin-holes, etc., are formed in the inorganic laminar compound-containing layer during the above "folding", the resultant oxygen permeability tends to be increased.

(Resin composition)

With respect to the composition ratio (volume ratio) between the inorganic laminar compound and the resin used in the present invention, the volume ratio of inorganic laminar compound/resin (ratio at the time of "Shikomi" (mixing for preparation)) may preferably be in the range of 5/95 to 90/10, more preferably in the range of 5/95 to 50/50 (particularly preferably, in the range of 10/90 to 30/70). The volume ratio in the range of 5/95 to 30/70 is advantageous in view of flexibility as a film or shaped article. When the volume ratio (fraction) of the above inorganic laminar compound/resin is below 5/95, the gas barrier property tends to be decreased. On the other hand, when the above volume ratio exceeds 90/10, the resultant film-forming property or formability tends to be decreased.

In view of the suppression of a decrease in the barrier property due to folding, the volume ratio may preferably be not less than 7/93. On the other hand, in view of the flexibility or the suppression of releasability of the resin composition layer from the base material, the volume ratio may preferably be not more than 17/83. In other words, the volume ratio of (inorganic laminar compound/resin) in the range of 7/93 to 17/83 is particularly preferred, because the decrease in the barrier property due to the folding may particularly be suppressed, and great peeling strength may easily be obtained in such a range.

Such a volume ratio may be determined by dividing respectively the numerator value (weight of the inorganic laminar compound) and the denominator value (weight of resin) constituting the weight ratio at the time of the "mixing for preparation" of these components, by respective densities. In general, there can be a case wherein the density of a resin (e.g., polyvinyl alcohol) is somewhat different depending on the crystallinity thereof. In the above case, however, it is possible to calculate the volume ratio while assuming the crystallinity of the polyvinyl alcohol to be 50%.

(Production method)

The method of formulating or producing the above composition comprising an inorganic laminar compound and a resin is not particularly limited. In view of the homogeneity or easiness in handling at the time of the formulation, it is possible to adopt, e.g., a method (first method) wherein a solution obtained by dissolving a resin, and a dispersion obtained by preliminarily swelling or cleaving an inorganic laminar compound, are mixed with each other, and thereafter the solvent is removed; a method (second method) wherein a dispersion obtained by swelling or cleaving an inorganic laminar compound, is added to a resin, and thereafter the solvent is removed; a method (third method) wherein an inorganic laminar compound is added to a solution obtained by dissolving a resin to obtain a dispersion in which the inorganic laminar compound is swollen or cleft, and thereafter the solvent is removed; a method (fourth method) wherein an inorganic laminar compound and a resin are kneaded under heating; etc. In view of easiness in the provision of a large aspect ratio of the inorganic laminar compound, it is preferred to adopt the former three method (first to third methods).

In the former two methods (first to second methods), in view of improvement in the water resistance (barrier property after the water-resistance environmental test), it is preferred that the solvent is removed from the system and thereafter a thermal aging treatment is conducted at a temperature of not less than 110° C. and not more than 220° C. (more preferably, a temperature of not less than 130° C. and not more than 210° C.). The aging period of time is not particularly limited. In consideration of the necessity for a

film temperature to reach at least a set temperature, for example, it is preferred to adopt an aging time of not less than 1 sec. and not more than 100 min. (more preferably, about 3 sec. to 10 min.) in the case of a drying method using a heating medium-contact type dryer such as hot-air dryer, in view of a balance between the water resistance and productivity.

The heat source to be used in the above aging treatment is not particularly limited. For example, it is possible to apply any of various methods such as those utilizing heat roll contact, heat medium contact (air, oil, etc.) infrared heating, and microwave heating.

The effect of improving the water resistance may remarkably be enhanced in a case where at least one (more preferably, both) of conditions such that the resin is a highly hydrogen-bonding resin, and/or the inorganic laminar compound is a clay mineral having a swelling property, is satisfied.

(Substance having gas barrier property)

The laminate, laminate film or shaped article according to the present invention has a feature such that a layer (or portion) comprising a resin composition comprising the above-mentioned (inorganic laminar compound/resin) and a layer (or portion) comprising a substance having a gas barrier property are combined with each other. The gas barrier substance may preferably be a substance having a gas barrier property of not more than 30 cc/m²·day·atm, more preferably not more than 10 cc/m²·day·atm (particularly preferably, not more than 2 cc/m²·day·atm), in terms of oxygen permeability (barrier property of base material before surface treatment) under the condition of 30° C. and 60% RH (relative humidity).

The gas barrier substance usable in the present invention is not particularly limited, as long as it has a "gas barrier property" as described above. Preferred examples thereof may include: metals or oxides, ethylene-vinyl alcohol copolymer and/or polyvinylidene chloride, etc. Among these gas barrier substances, ethylene-vinyl alcohol copolymer and polyvinylidene chloride are substances having a film-forming property or film formability in itself.

(Metal or oxide)

In the present invention, in a case where a metal or oxide is used as a substance having a gas barrier property, the metal or oxide may preferably be used in the form of a layer or film. The "metal" to be used in such an embodiment is not particularly limited as long as it has a gas barrier property, but a metal having a stability in the air in the form of a film or thin film may preferably be used. In view of the stability in the air, it is preferred to use a metal (such as aluminum) such that the film surface is stabilized due to oxidation after the thin film formation.

On the other hand, the above-mentioned oxide is not particularly limited as long as it has a gas barrier property. Preferred examples of such an oxide may include: aluminum oxide, silicon oxide, titanium oxide, zinc oxide, etc.

In view of a balance between the gas barrier property and flexibility (or productivity), the film of the metal or oxide to be used in the present invention may preferably have a thickness of not less than 1 nm and not more than 1000 nm, more preferably not less than 10 nm and not more than 300 nm (particularly preferably, not less than 15 nm and not more than 150 nm).

The process for forming a film of the metal or oxide to be used in the present invention is not particularly limited. It is possible to use a vapor-phase deposition such as ordinary vacuum evaporation, CVD (chemical vapor deposition), and sputtering; and liquid-phase deposition such as sol-gel process.

In the present invention, the above-mentioned film of a metal or oxide may be formed on at least one surface side of a "resin film". The resin film to be used for such a purpose is not particularly limited. In view of the film strength, however, it is preferred to use, e.g., a biaxially oriented polyethylene terephthalate film, a biaxially oriented nylon film, a biaxially oriented polypropylene film, etc.

(Ethylene-vinyl alcohol copolymer)

In the present invention, in a case where the above-mentioned ethylene-vinyl alcohol copolymer is used as a gas barrier substance, it is preferred to use, as the ethylene-vinyl alcohol copolymer, a product obtained by co-polymerizing ethylene and vinyl acetate and then saponifying the resultant copolymerization product. The mole fraction of ethylene in such a case may preferably be in the range of 20–60 mol % (more preferably, 25–50 mol %). The method of forming the ethylene-vinyl alcohol copolymer into a film is not particularly limited. For example, it is possible to use ordinary extrusion molding such as inflation molding, casting or coating from emulsion, etc. The thickness of the film is not particularly limited, but may preferably be about 0.5–50 μm (more preferably, about 1–30 μm). In the case of extrusion-molded film, it is preferred to use a film which has been subjected to orientation treatment, in view of the film strength.

(Polyvinylidene chloride)

In the present invention, in a case where polyvinylidene chloride is used as the gas barrier substance, it is possible to use a polymer predominantly comprising a vinylidene chloride monomer (preferably, one having a mole fraction of vinylidene chloride monomer of 70 mol % or more, more preferably, 80 mol % or more) without particular limitation. The polyvinylidene chloride may also contain at least one of various kinds of copolymerization monomers, as desired.

The method of forming the polyvinylidene chloride into a film is not particularly limited. It is preferred to use ordinary extrusion molding using a T-type die, coating (so-called "K-coating") utilizing polyvinylidene chloride in an aqueous emulsion or solution form, etc. The thickness of the film is not particularly limited, but may preferably be about 0.5–50 μm (more preferably, about 1–30 μm). In the case of an extrusion film, it is preferred to use a film which has been subjected to orientation treatment, in view of film strength.

(Method of lamination onto gas barrier substance layer)

The method by which a layer of a resin composition containing an inorganic laminar compound is laminated on the above-mentioned layer of the gas barrier substance (such as thin film of metal or oxide, layer of ethylene-vinyl alcohol copolymer, and layer of polyvinylidene chloride) is not particularly limited. It is preferred to use a coating method wherein a coating liquid containing a resin composition is applied onto the surface of a base material or a layer of a gas barrier substance, and then dried and heat-treated; a method wherein a layer of a resin composition containing an inorganic laminar compound is laminated afterward onto a gas barrier substance layer; etc. The interface between the gas barrier substance layer and the resin composition layer may be subjected to treatment such as corona treatment and anchor coating treatment, as desired.

Specific examples of the coating method may include: gravure methods such as direct gravure method, reverse gravure method and micro-gravure method; roll coating methods such as twin-roll bead coating method, and bottom-feed triple reverse coating method; doctor knife method, die coating method, dip coating method, bar coating method, and coating method combining these coating methods.

(Laminate structure)

The laminate structure or shaped structure to be used in the present invention is not particularly limited, as long as it comprise, as at least a portion (or layer) thereof, a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000. More specifically, the laminate or resin composition according to the present invention may be shaped into any of various forms such film, sheet, and container.

FIG. 4 is a schematic sectional view showing an embodiment wherein the laminate according to the present invention is shaped into the form of a laminate film. Referring to FIG. 4, the laminate film in this embodiment comprises a resin film 3, a layer 2 of a gas barrier substance disposed on the resin layer 3, and an inorganic laminar compound-containing (resin composition) layer 1 disposed on the gas barrier substance layer 2.

The laminate film according to the present may also have a laminate structure as shown in the schematic sectional views of FIGS. 5-7 as desired, in consideration of a balance between the gas barrier property, and mechanical strength such as film strength as the laminate. The laminate film in the embodiment of FIG. 5 further comprises a "base material 4 for lamination" on the inorganic laminar compound-containing layer 1 in the embodiment of the above FIG. 4. The laminate film in the embodiment of FIG. 6 further comprises a "base material 4 for lamination" on the resin film 3 in the embodiment of the above FIG. 4. In addition, the laminate film in the embodiment of FIG. 7 further comprises a "base material 4 or 4a for lamination" both on the inorganic laminar compound-containing layer 1 side, and on the resin film 3 side in the embodiment of the above FIG. 4.

In a case where the above gas barrier substance itself has a film-forming property (e.g., in a case where the gas barrier substance comprises a resin such as ethylene-vinyl alcohol copolymer, and polyvinylidene chloride), the laminate according to the present invention may have a structure as shown in FIG. 8. Referring to FIG. 8, the laminate film in this embodiment comprises a layer 2a of a gas barrier substance, and an inorganic laminar compound-containing (resin composition) layer 1 disposed on the gas barrier substance layer 2a.

In such an embodiment, the laminate may also have a laminate structure as shown in schematic sectional views of FIGS. 9-11 as desired, in consideration of a balance between the gas barrier property, and mechanical strength such as film strength as a laminate. The laminate film in the embodiment of FIG. 9 further comprises a base material 13 for laminating on the inorganic laminar compound-containing layer 1 of the embodiment of above FIG. 8. The laminate film in the embodiment of FIG. 10 further comprises a base material 13 for laminating on the gas barrier substance layer 2a side of the embodiment of the above FIG. 8. In addition, the laminate film in the embodiment of FIG. 11 further comprises a base material 13 or 13a for laminating both on the inorganic laminar compound-containing layer 1 side and on the gas barrier substance layer 2a side in the embodiment of above FIG. 8.

(Base material)

In the present invention, the base material to be used for the base material (or substrate) layer (e.g., the resin film 3 in the embodiment of FIG. 4) is not particularly limited. It is possible to use any of known or ordinary base materials such as resin, paper, aluminum foil, woody material, cloth, and nonwoven fabric, in accordance with the use or purpose thereof.

Specific examples of the resin constituting the base material may include: polyolefin-type resins such as polyethylene (low density, high density) ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, and ionomer resin; polyester-type resins such as polyethylene terephthalate (PET), polybutylene terephthalate, and polyethylene naphthalate; amide-type resins such as nylon-6, nylon-6-6, meta-xylenediamine-adipic acid condensation polymer, and polymethyl methacrylimide; acrylic-type resins such as polymethyl methacrylate; styrene- or acrylonitrile-type resins such as polystyrene, styrene-acrylonitrile copolymer, styrene-acrylonitrile-butadiene copolymer, and polyacrylonitrile; hydrophobicity-imparted cellulose-type resins such as cellulose triacetate, and cellulose diacetate; halogen-containing resins such as polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, and polytetrafluoroethylene (Teflon); hydrogen-bonding resins such as polyvinyl alcohol, ethylene-vinyl alcohol copolymer and cellulose derivatives; engineering plastic-type resins such as polycarbonate resin, polysulfone resin, polyethersulfone resin, polyether ether ketone resin, polyphenylene oxide resin, polymethylene oxide resin, and liquid crystal resin; etc.

In a case where the laminate according to the present invention is shaped into a film form, as the outside layer (a layer constituting the outside of the laminate, e.g., the layer 3 or 4 in the embodiment of FIG. 5, the layer 4a in the embodiment of FIG. 7), it is preferred to dispose biaxially oriented polypropylene, polyethylene terephthalate, and nylon, biaxially oriented polypropylene, polyethylene terephthalate, and nylon having a polyvinylidene chloride coating (so-called "K-coat"), etc. On the other hand, as the inside layer (a layer constituting the inside or content side of the laminate, e.g., the layer 3 or 4 in the embodiment of FIGS. 4-5, the layer 4 or 4a in the embodiment of FIG. 6-7), it is preferred to dispose a resin having a good heat sealing property, such as polyolefin-type resin. Specific examples of such a polyolefin-type resin may include: polyethylene (low density, high density) ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, ionomer resin, etc.

(Resin composition layer)

The thickness of a resin composition comprising an inorganic laminar compound and a resin is not particularly limited. While the thickness of this resin composition layer is somewhat different depending on the kind of a base material to be combined therewith, or an intended barrier performance, the thickness may preferably be not more than 10 μm in terms of the thickness after drying. In a case where a higher transparency is demanded, the thickness may preferably be not more than 2 μm (more preferably, not more than 1 μm) in terms of thickness after drying. When the thickness is not more than 1 μm , it is considerably advantageous in view of the transparency as the resultant laminate. Accordingly, such a thickness is particularly preferred for a use wherein transparency is particularly demanded (e.g., use for food packaging).

The thickness of the resin composition layer does not have a particular lower limit. In view of provision of a sufficient gas barrier property, the thickness may preferably be 1 nm or larger, more preferably 10 nm or larger (particularly preferably, 100 nm or larger).

(Additive)

In addition, it is also possible to mix with or add to the laminate or laminate film according to the present invention as desired, any of various additives such as ultraviolet light absorbing agent, colorant, and antioxidant, within a range wherein the effect of the present invention is not substantially impaired. Further, it is of course possible to use an adhesive or printing ink, as desired, e.g., at the time of laminating operation.

In the present invention, the shape or form of a product is not particularly limited as long as it comprises, as at least a layer (or a portion) thereof, the above-mentioned laminate or laminate film according to the present invention. More specifically, the product may be any of various forms inclusive of laminate, or shaped or molded product (e.g., container or vessel such as bottle, tray, and cup), etc.

Hereinbelow, the present invention will be described in detail with reference to Examples, by which the present invention is not limited.

(Examples)

The methods of measuring various physical properties used in the present specification are described below.

<Oxygen permeability>

Oxygen permeability was measured by using a method according to Japanese Industrial Standard (JIS) (JIS K-7126).

More specifically, a sample film (test piece) was mounted to a commercially available oxygen permeability measuring apparatus (trade name: OX-TRAN 10/50A, mfd. by MOCON Co. U.S.A.), and the oxygen permeability was measured under the measuring conditions of a temperature of 31° C. (humidity-controlled thermostat=21° C.). At this time, the relative humidity was about 61%. In this measurement, the oxygen permeability of the sample film was continuously measured, and the oxygen permeability at a point of time at which the oxygen permeability became substantially constant (usually, about several hours to three days after the initiation of the measurement) was used as the data thereof in this specification. When the oxygen transmission is represented by the ordinate of a graph, and the time t is represented by the abscissa thereof, the period of time (θ sec.) wherein the film interior reaches the equilibrium may be represented by an equation of $\theta = d^2/6D$, wherein d denotes the film thickness (μm) of the film, and D denotes a diffusion constant ($(\mu\text{m})^2/\text{sec}$). Accordingly, the period of time for the measurement is different depending on the kind of the sample.

<Thickness measurement>

A thickness of not less than 0.5 μm was measured by means of a commercially available digital-type thickness measuring device (contact-type thickness measuring device, trade name: Ultra-High Precision Deci-Micro Head MH-15M, mfd. by Nihon Kogaku K.K.).

On the other hand, a thickness of less than 0.5 μm was determined by a gravimetric analysis method, wherein the weight of a film having a predetermined area was measured, the resultant weight was divided by the area, and further divided by the specific gravity of the composition, or an elemental analysis method (in the case of a laminate comprising a resin composition and a base material, etc.).

In a case where the elemental analysis (Measuring principle: ICP emission spectrometry, with reference to a book entitled "ICP Emission Spectrometry", edited by Nihon Bunseki Kagaku-kai (Japan Society of Analytical Chemistry), 1988, published by Kyoritsu Shuppan) was used, the ratio between the layer of the resin composition according to the present invention and the base material was

determined by calculation on the basis of the ratio between the analytical value of a predetermined inorganic element (originating from the composition) of the laminate, and the fraction of a predetermined element (e.g., Si) of the layer of the inorganic laminar compound alone.

<Particle size measurement>

Predetermined parameters such as the refractive index of a solvent (e.g., $n=1.332$ in the case of water), the viscosity of the solvent (e.g., $\eta=0.890$ cP in the case of water), and the refractive index of an inorganic laminar compound (e.g., $n=1.56$ in the case of mica) were inputted to a commercially available ultrafine particle size analyzing apparatus (trade name: BI-90, mfd. by Brookhaven Co., U.S.A., Japanese agent: Nikkiso K.K.), and measurement was conducted at a temperature of 25° C. in a solvent of water, while a solution having a weight ratio (inorganic laminar compound/water) of 2% was diluted in accordance with an estimated particle size. Through such a method, the particle size L was determined as a central particle size value measured by photon correlation method based on dynamic light scattering, which was automatically output from the above analyzer as a digital value. In this particle size measurement for the inorganic laminar compound, each time the measurement was conducted, calibration measurement was also conducted by using the following standard samples comprising true spherical fine particles, whereby it was confirmed that the measured data of the particle size of the standard samples fell within the range of relative error of $\pm 10\%$.

True Spherical Fine Particles: particles mfd. by Dow Chemical Co., U.S.A., trade name: UNIFORM LATEX PARTICLES

<Particle size determined by SEM (scanning electron microscope); Dow>

0.085 μm (deviation 0.0055 μm)

0.109 μm (deviation 0.0027 μm)

0.330 μm (deviation 0.0040 μm)

0.806 μm (deviation 0.0057 μm)

2.02 μm (deviation 0.0135 μm)

2.97 μm (deviation 0.23 μm)

<Aspect ratio calculation>

An inorganic laminar compound and a resin composition were respectively subjected to diffraction measurement by means of a commercially available X-ray diffractometer (trade name: XD-5A, mfd. by Shimadzu Seisakusho K.K.) through a powder method. The lattice spacing (unit thickness) a was determined on the basis of the measurement of the inorganic laminar compound alone. In addition, it was confirmed that a portion in which the lattice spacing of the inorganic laminar compound had been increased (a portion in which lattice spacing $d > a$) was present, on the basis of the diffraction measurement of the resin composition.

By use of the resultant particle size L obtained by the dynamic scattering method, the aspect ratio Z was determined by using an equation of $Z=L/a$.

EXAMPLE 1

Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo K.K.) was dispersed in ion-exchange water (electric conductivity: 0.7 $\mu\text{S}/\text{cm}$ or below) so as to provide a concentration of 2 wt. %, thereby to provide a dispersion of an inorganic laminar compound (Liquid A). The above montmorillonite had a particle size of 560 nm, a unit thickness a obtained by powder X-ray diffraction of 1.2156 nm, and an aspect ratio of 461.

Separately, a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree

of polymerization=1700) was dissolved in ion-exchange water (electric conductivity: 0.7 μ S/cm or below) so as to provide a concentration of 2 wt. %, thereby to provide a resin solution (Liquid B).

The thus obtained Liquids A and B were mixed with each other so as to provide a solid content ratio (volume ratio) of (inorganic laminar compound/resin) =3/7, thereby to provide a coating liquid.

The coating liquid having the above composition was applied onto the vapor-deposited silicon oxide surface of a 12 μ m-thick polyethylene terephthalate film having a silicon oxide vapor deposition coating (trade name: MOS, mfd. by Oike Kogyo Co.) by gravure coating (by use of "Test Coater" mfd. by Yasui Seiki K.K., microgravure coating method, coating speed: 3 m/min., drying temperature: 80° C. (inlet side heater), 100° C. (outlet side heater)), thereby to provide a laminate film. The thickness after drying of the above coating layer was 0.3 μ m.

The thus obtained laminate film was subjected to oxygen permeability measurement at 30° C., 60% RH. As a result, the measured oxygen permeability was below 0.1 cc/m²·day·atm as shown in Table 1, and it was found that the laminate film was excellent in gas barrier property.

EXAMPLES 2-6

Laminate films were prepared and the oxygen permeabilities thereof were measured in the same manner as in Example 1, except that the kind of the inorganic laminar compound and/or resin, volume ratio between the inorganic laminar compound and resin, crosslinking agent for a hydrogen-bonding group, and the conditions for a heat treatment after the film formation were respectively changed to those shown in Table 1.

The measurement results are shown in the above Table 1. As shown in the Table 1, all of the laminate films provided by these Examples had an excellent barrier property.

EXAMPLE 7

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 1 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol. By use of the resultant mixture, a laminate film was prepared and the oxygen permeability thereof was measured in the same manner as in Example 1, except that the other constituents were changed to those as shown in Table 1.

The measurement results are shown in the above Table 1. As shown in the Table 1, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 8

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising Liquid A and Liquid B prepared in Example 1 in an amount so as to provide a ratio of the zirconium element of one mole with respect to 15 mole of the hydroxyl group of the Polyvinyl alcohol. By use of the resultant mixture, a

laminate film was prepared in the same manner as in Example 1, except that the other constituents were changed to those as shown in Table 1. Thereafter, the resultant laminate film was subjected to a heat treatment by means of a hot-air dryer at 140° C. for 10 min., thereby to provide a laminate film.

The oxygen permeability of the thus obtained was measured. As shown in the above Table 1, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 9

A 33 cm-wide non-oriented polypropylene film (trade name: Pyren Film-CT, mfd. by Toyobo K.K., thickness 60 μ m) was dry-laminated onto an inorganic laminar compound-containing layer (resin composition layer) side of the laminate film obtained in Example 1, by means of a laminating machine (trade name: Test-Coater, mfd. by Yasui Seiki Co.) under a pressure of 4 kg/cm² at a speed of 6 m/min., while using a urethane-type adhesive (trade name: Yunoflex-J3, mfd. by Sanyo Kasei K.K.) in an amount of 3 g/m² (solid content), thereby to provide a laminate film. The oxygen permeability of the thus obtained laminate film was then measured at 30° C., 60% RH. As a result, the oxygen permeability was below 0.1 cc/m²·day·atm and it was also found that the laminate film was excellent in the heat sealing property and transparency, as well as the gas barrier property.

Comparative Example 1

A laminate film was prepared in the same manner as in Example 1, except that the dispersion of the inorganic laminar compound (Liquid A) used in Example 1 was not used, and a resin solution (Liquid B) obtained by dissolving a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree of polymerization=1700) in ionexchange water so as to provide a concentration of 2 wt. %, was used alone as a coating liquid.

The oxygen permeability of the thus obtained laminate film was measured. The measurement results are shown in Table 1. As shown in the Table 1, the above laminate film only had a poor gas barrier property.

Comparative Examples 2-4

The oxygen permeabilities of some commercially available metal- or oxide-vapor deposited films as shown in the above Table 1 were measured.

As shown in the Table 1, these films only had a poor gas barrier property.

Comparative Example 5

Preparation of a laminate film was attempted in the same manner as in Example 1, except that the resin solution (Liquid B) used in Example 1 was not used, and the dispersion of the inorganic laminar compound (Liquid A) used in Example 1 was used alone as a coating liquid. As a result, in this preparation procedure, the powder of the inorganic laminar compound (natural montmorillonite) was partially peeled off from the laminate film, the resultant surface the laminate film showed a noticeable whitish color (outside haze or scratches originating from the surface unevenness), and a good laminate film could not be obtained.

The meanings of the abbreviation used in the above Table 1 are as follows.

MOS: Polyethylene terephthalate film having a silicon oxide vapor deposition coating (trade name: MOS, mfd. by Oike Kogyo Co.)

VMPET: Polyethylene terephthalate film having an aluminum oxide vapor deposition coating (trade name: VMPET, mfd. by Toyo Aluminum K.K.)

AL: Polyethylene terephthalate film having an aluminum vapor deposition coating (trade name: Tetlite, mfd. by Oike Kogyo Co.)

F: Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo Co.)

H: Polyvinyl alcohol (trade name: Poval 117H, mfd. by Kuraray K.K., degree of polymerization=1700, saponification degree=99.6%.)

Z: Aqueous solution of zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K.)

A: Heat treating of a laminate film (after drying) at 140° C., for 10 min.

EXAMPLE 10

Synthetic mica (tetrasilic mica, trade name: NA-TS, mfd. by Topy Kogyo Co.) was dispersed in ion-exchange water (electric conductivity: 0.7 μ S/cm or below) so as to provide a concentration of 0.65 wt. %, thereby to provide a dispersion of an inorganic laminar compound (Liquid A). The above synthetic mica had a particle size of 977 nm, a unit thickness a obtained by powder X-ray diffraction of 0.9557 nm, and an aspect ratio Z of 1043.

Separately, a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree of polymerization=1700) was dissolved in ion-exchange water (electric conductivity: 0.7 μ S/cm or below) so as to provide a concentration of 0.325 wt. %, thereby to provide a resin solution (Liquid B).

The thus obtained Liquids A and B were mixed with each other so as to provide a solid content ratio (volume ratio) of (inorganic laminar compound/resin) =3/7, thereby to provide a coating liquid.

The coating liquid having the above composition was applied onto a 15 μ m-thick ethylene-vinyl alcohol copolymer film (trade name: Eval EF-F, mfd. by Kuraray K.K.) by gravure coating (by use of "Test Coater" mfd. by Yasui Seiki K.K., microgravure coating method, coating speed: 3 m/min., drying temperature: 80° C. (inlet side heater), 100° C. (outlet side heater)), thereby to provide a laminate film. The thickness after drying of the above coating layer was 0.8 μ m.

The thus obtained laminate film was subjected to oxygen permeability measurement at 30° C., 60% RH. As a result, the measured oxygen permeability was 0.09 cc/m²·day·atm as shown in Table 2.

EXAMPLES 11-15

Laminate films were prepared and the oxygen permeabilities thereof were measured in the same manner as in Example 10, except that the kind of the inorganic laminar compound and/or resin, volume ratio between the inorganic laminar compound and resin, crosslinking agent for a hydrogen-bonding group, and heat treatment after the film formation were respectively changed to those shown in Table 2.

The measurement results are shown in the above Table 2. As shown in the Table 2, all of the laminate films provided by these Examples had an excellent barrier property.

EXAMPLE 16

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 10 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol. By use of the resultant mixture, a laminate film was prepared and the oxygen permeability thereof was measured in the same manner as in Example 10, except that the other constituents were changed to those as shown in Table 2.

The measurement results are shown in the above Table 2. As shown in the Table 2, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 17

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 10 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol. By use of the resultant mixture, a laminate film was prepared in the same manner as in Example 10, except that the other constituents were changed to those as shown in Table 2. Thereafter, the resultant laminate film was subjected to a heat treatment by means of a hot-air dryer at 140° C. for 10 min., thereby to provide a laminate film.

The oxygen permeability of the thus obtained laminate film was measured. As shown in the Table 2, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 18

A non-oriented polypropylene film (trade name: Pyren Film-CT, mfd. by Toyobo K.K., thickness 60 μ m) was dry-laminated onto an inorganic laminar compound-containing layer (resin composition layer) side of the laminate film obtained in Example 10 in the same manner as in Example 9, while using a urethane-type adhesive (trade name: Yunoflex-J3, mfd. by Sanyo Kasei K.K.) in an amount of 3 g/m² (solid content), thereby to provide a laminate film. The oxygen permeability of the thus obtained laminate film was then measured at 30° C., 60% RH. As a result, the oxygen permeability was below 0.1 cc/m²·day·atm, and it was also found that the laminate film was excellent in the heat sealing property and transparency, as well as the gas barrier property.

Comparative Example 6

A laminate film was prepared in the same manner as in Example 10, except that the dispersion of the inorganic laminar compound (Liquid A) used in Example 10 was not used, and a resin solution (Liquid B) obtained by dissolving a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree of polymerization=1700) in ion-exchange water so as to provide a concentration of 1 wt. %, was used alone as a coating liquid.

The oxygen permeability of the thus obtained laminate film was measured. The measurement results are shown in Table 2. As shown in the Table 2, the above laminate film only had a poor gas barrier property.

Comparative Example 7

A commercially available 15 μm -thick ethylene-vinyl alcohol copolymer film (trade name: Eval EF-F, mfd. by Kuraray K.K.) was subjected to a test for measuring the oxygen permeability thereof.

As shown by the measurement results in the Table 2, this film only had a poor gas barrier property.

Comparative Example 8

Preparation of a laminate film was attempted in the same manner as in Example 10, except that the resin solution (Liquid B) used in Example 1 was not used, and the dispersion of the inorganic laminar compound (Liquid A) used in Example 10 was used alone as a coating liquid. As a result, in this preparation procedure, the powder of the inorganic laminar compound (synthetic mica) was partially peeled off from the laminate film, the resultant surface the laminate film showed noticeable scratches, and a good laminate film could not be obtained.

The meanings of the abbreviation used in the above Table 2 are as follows.

EF-F: Ethylene-vinyl alcohol copolymer film (trade name: Eval EF-F, mfd. by Kuraray K.K., ethylene content=32 mol %)

EF-E: Ethylene-vinyl alcohol copolymer film (trade name: Eval EF-E, mfd. by Kuraray K.K., ethylene content=44 mol %)

NA: Tetrasilylic mica (trade name: NaTS, mfd. by Topy Kogyo Co.)

F: Natural montmorillonite (trade name: Kunipia F, by Kunimine Kogyo Co.)

H: Polyvinyl alcohol (trade name: Poval 117H, mfd. by Kuraray K.K., degree of polymerization=1700, saponification degree=99.6%,)

Z: Aqueous solution of zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K.)

A: Heat treating of a laminate film (after drying) at 140° C., for 10 min.

EXAMPLE 19

Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo K.K.) was dispersed in ion-exchange water (electric conductivity: 0.7 $\mu\text{S}/\text{cm}$ or below) so as to provide a concentration of 2 wt. %, thereby to provide a dispersion of an inorganic laminar compound (Liquid A). The above montmorillonite had a particle size of 560 nm, a unit thickness a obtained by powder X-ray diffraction of 1.2156 nm, and an aspect ratio of 461.

Separately, a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree of polymerization=1700) was dissolved in ion-exchange water (electric conductivity: 0.7 $\mu\text{S}/\text{cm}$ or below) so as to provide a concentration of 2 wt. %, thereby to provide a resin solution (Liquid B).

The thus obtained Liquids A and B were mixed with each other so as to provide a solid content ratio (volume ratio) of (inorganic laminar compound/resin)=3/7, thereby to provide a coating liquid.

The coating liquid having the above composition was applied onto a corona-treated surface of a 25 μm -thick biaxially oriented polypropylene film having a polyvinylidene chloride coating (trade name: Senesee KOP, mfd. by Daicel K.K., polyvinylidene chloride layer: about 4 μm) by gravure coating (by use of "Test Coater" mfd. by Yasui Seiki K.K., microgravure coating method, coating speed: 3 m/min., drying temperature: 80° C. (inlet side heater), 100° C. (outlet side heater)), thereby to provide a laminate film. The thickness after drying of the above coating layer was 0.5 μm .

The thus obtained laminate film was subjected to oxygen permeability measurement at 30° C., 60% RH. As a result, the measured oxygen permeability was below 0.1 cc/m²·day·atm as shown in Table 3, and it was found that the laminate film was excellent in gas barrier property.

EXAMPLES 20-24

Laminate films were prepared and the oxygen permeabilities thereof were measured in the same manner as in Example 19, except that the kind of the inorganic laminar compound and/or resin, volume ratio between the inorganic laminar compound and resin, crosslinking agent for a hydrogen-bonding group, and heat treatment after the film formation were respectively changed to those shown in Table 3.

The measurement results are shown in Table 3. As shown in the Table 3, all of the laminate films provided by these Examples had an excellent barrier property.

EXAMPLE 25

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 19 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol. By use of the resultant mixture, a laminate film was prepared and the oxygen permeability thereof was measured in the same manner as in Example 19, except that the other constituents were changed to those as shown in Table 3.

The measurement results are shown in the above Table 3. As shown in the Table 3, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 26

Zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 19 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol. By use of the resultant mixture, a laminate film was prepared in the same manner as in Example 19, except that the other constituents were changed to those as shown in Table 3. Thereafter, the resultant laminate film was subjected to a heat treatment by means of a hot-air dryer at 140° C. for 10 min., thereby to provide a laminate film.

The oxygen permeability of the thus obtained laminate film was measured. As shown in the Table 3, the laminate film provided by this Example had an excellent barrier property.

EXAMPLE 27

A non-oriented polypropylene film (trade name: Pyren Film-CT, mfd. by Toyobo K.K., thickness 60 μ m) was dry-laminated onto an inorganic laminar compound containing layer (resin composition layer) side of the laminate film obtained in Example 19 in the same manner as in Example 9, while using a urethane-type adhesive (trade name: Yunoflex-J3, mfd. by Sanyo Kasei K.K.) in an amount of 3 g/m² (solid content), thereby to provide a laminate film. The oxygen permeability of the thus obtained laminate film was then measured at 30° C., 60% RH. As a result, the oxygen permeability was below 0.1 cc/m²·day·atm as shown in Table 3, and it was also found that the laminate film was excellent in the heat sealing property and transparency, as well as the gas barrier property.

Comparative Example 9

A laminate film was prepared in the same manner as in Example 19, except that the dispersion of the inorganic laminar compound (Liquid A) used in Example 19 was not used, and a resin solution (Liquid B) obtained by dissolving a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K.K., saponification degree=99.6%, degree of polymerization=1700) in ion-exchange water so as to provide a concentration of 2 wt. %, was used alone as a coating liquid.

The oxygen permeability of the thus obtained laminate film was measured. The measurement results are shown in Table 3. As shown in the Table 3, the above laminate film only had a poor gas barrier property.

Comparative Example 10

The oxygen permeabilities of some commercially available metal- or oxide-vapor deposited films as shown in above Table 3 were measured.

As shown in the Table 3, these films only had a poor gas barrier property.

Comparative Example 11

Preparation of a laminate film was attempted in the same manner as in Example 19, except that the resin solution (Liquid B) used in Example 19 was not used, and the dispersion of the inorganic laminar compound (Liquid A) used in Example 19 was used alone as a coating liquid. As a result, in this preparation procedure, the powder of the inorganic laminar compound (natural montmorillonite) was partially peeled off from the laminate film, the resultant surface the laminate film showed noticeable scratches, and a good laminate film could not be obtained.

The meanings of the abbreviation used in the above Table 3.

KOP: Biaxially oriented polypropylene film having a polyvinylidene chloride coating (trade name: Senesee KOP, mfd. by Daicel K.K., polyvinylidene chloride layer : about 4 μ m)

KET: Biaxially oriented polyethylene terephthalate film having a polyvinylidene chloride coating (trade name: Senesee KET, mfd. by Daicel K.K., polyvinylidene chloride layer : about 4 μ m)

F: Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo Co.)

H: Polyvinyl alcohol (trade name: Poval 117H, mfd. by Kuraray K.K., degree of polymerization=1700, saponification degree=99.6%,)

Z: Aqueous solution of zirconium ammonium carbonate (trade name: Zircosol AC7, mfd. by Dai-ichi Kigenso Kogyo K.K.)

A: Heat treating of a laminate film (after drying) at 140° C., for 10 min.

FIGS. 12-17 respectively show powder X-ray diffraction peaks of an inorganic laminar compound or resin composition each having various values of the lattice spacing d.

FIG. 12 is a graph showing X-ray diffraction peaks of a polyvinyl alcohol PVA-117H/"Kunipia F" composition used in the above Examples. FIG. 13 is a (montmorillonite) used in Examples.

FIG. 14 (composition having a lattice spacing d=19.62 Å (pattern of the above FIG. 2), FIG. 15 (composition having a lattice spacing d=32.94 Å, pattern of the above FIG. 2 or FIG. 3), FIG. 16 (composition having a lattice spacing d \geq 44.13 Å (composition having a pattern of the above FIG. 3), and FIG. 17 (composition having a lattice spacing d \geq 44.13 Å, pattern of the above FIG. 3) are graphs respectively showing powder X-ray diffraction peaks of resin compositions having various values of the lattice spacing d.

INDUSTRIAL APPLICABILITY

As described hereinabove, according to the present invention, there is provided a laminate, laminate film or shaped article comprising: at least, a layer having a gas barrier property, and a resin composition layer containing an inorganic laminar compound having an aspect ratio of not less than 500 and not more than 5000.

According to the present invention, there is obtained a gas barrier property at a high level which has never been achieved in the prior art, on the basis of the combination of the above-mentioned resin composition layer containing the inorganic laminar compound having a specific aspect ratio, and the gas barrier substance layer.

In an embodiment of the present invention wherein an ethylene-vinyl alcohol copolymer (or polyvinylidene chloride) is used as the gas barrier substance, as shown in the "Best Mode for carrying Out the invention" and "Examples", the present invention easily provides a very low oxygen permeability which is lower than that in the prior art by one figure (digit) or two figures under a standard environment, while a layer of the ethylene-vinyl alcohol copolymer alone only shows an oxygen permeability at a level of about 1 cc/m²·day·atm (in the case of a layer predominantly comprising polyvinylidene chloride alone, at a level of about 10 cc/m²·day·atm). As a result, the present invention provides a barrier property which is much higher than the barrier property of a material of a similar kind used in the prior art.

According to the present invention, it is possible to remarkably suppress a decrease in the "barrier property at the time of folding", which has been liable to occur when a metal or oxide film is laminated on a resin composition.

The laminate, laminate film or shaped article according to the present invention may exhibits a barrier property at a level which is much higher than the barrier property of a material of a similar kind used in the prior art, and is even closer to that of metal or ceramic. On the basis of such a high barrier property, the laminate, laminate film or shaped article according to the present invention is also usable for a purpose in which a metal or inorganic material such as aluminum foil and glass is considered to be essential in the prior art, and is a material overthrowing the common knowledge on the conventional resin composition having a barrier

property. Of course, in consideration of the weak points such as opaqueness of a metal and brittleness of a ceramic material, the laminate, laminate film or shaped article according to the present invention comprising a resin composition has characteristics better than those of the metal or ceramic material.

On the basis of the above-mentioned characteristics, the laminate, laminate film or shaped article according to the present invention is usable as a packaging material. In the usage in food packaging, it is usable for a wide range of packaging, such as: "miso" (soybean paste), pickles, daily dish, baby food, "tsukudani" (preserved food boiled down in soy sauce), "konnyaku" (paste made from devil's-tongue), "chikuwa" (Japanese fish paste cooked in a bamboo-like shape), "kamaboko" (boiled fish paste), processed marine products, meat ball, hamburger steak, Genghis Khan-type meat (meat for cooking), ham, sausage, and other processed stock raising products, green tea, coffee, tea, dried bonito, "tororo-konbu" (sliced tangle), oily confectionery such as French fried potatoes and buttered peanuts, confectionery made from rice, biscuit, cookie, cake, "manjuu" (bun stuffed with sweetened bean paste), sponge cake, cheese, butter, cut rice cake, soup, source, Chinese noodles, etc.

In addition, the laminate, laminate film or shaped article according to the present invention is suitably usable for a wide range purposes including industrial packaging such as: those in the fields of medical, electronics, chemical and mechanical; more specifically, packaging of feed for pets, agricultural chemicals and fertilizer, and package for trans-fusion; and semiconductor packaging, packaging of an oxidative agent (or an agent susceptible to oxidation), precision material packaging, etc.

Further, the laminate, laminate film or shaped article according to the present invention is suitably usable as a shaped article in the form of bottle, tray, etc., to be used for a squeezing-type bottle of mayonnaise, juice, soy sauce, edible oil, sauce, food tray for microwave oven, cups for yogurt, etc.

The laminate, laminate film or shaped article according to the present invention may exhibit a good gas barrier property in any form or shape of those as described hereinabove.

TABLE 1

	BASE MATERIAL (THICKNESS μm)	INORGANIC SUBSTANCE- CONTAINING LAYER [VOLUME RATIO] (THICKNESS μm)	OXYGEN PERMEABILITY (30° C., 60% RH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$
EX. 1	MOS (12)	F/H[3/7] (0.3)	<0.1
EX. 2	VMPET (12)	F/H[3/7] (0.3)	<0.1
EX. 3	VMPET (12)	F/H[4/6] (0.3)	<0.1
EX. 4	AL (12)	F/H[2/8] (0.3)	<0.1
EX. 5	MOS (12)	F/H[1.5/8] (0.3)	<0.1
EX. 6	MOS (12)	F/H[1/8] (0.5)	<0.1
EX. 7	MOS (12)	F/H[2/8] (0.8) Z	<0.1
EX. 8	MOS (12)	F/H[1.5/8] (0.8) ZA	<0.1
COMP. EX. 1	MOS (12)	H (0.5)	0.3
COMP. EX. 2	MOS (12)	NONE	5.0
COMP. EX. 3	VMPET (12)	NONE	6.2
COMP. EX. 4	AL (12)	NONE	0.9

TABLE 2

	BASE MATERIAL (THICKNESS μm)	INORGANIC SUBSTANCE- CONTAINING LAYER [VOLUME RATIO] (THICKNESS μm)	OXYGEN PERMEABILITY (30° C., 60% RH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$
EX. 10	EF-F (15)	NA/H[3/7] (0.8)	<0.1
EX. 11	EF-F (15)	F/H[3/7] (0.8)	<0.1
EX. 12	EF-E (15)	F/H[4/6] (0.8)	<0.1
EX. 13	EF-E (15)	F/H[2/8] (0.8)	<0.1
EX. 14	EF-F (15)	F/H[1.5/8] (0.9)	<0.1
EX. 15	EF-F (15)	F/H[1/8] (1.3)	<0.1
EX. 16	EF-F (15)	F/H[2/8] (0.8) Z	<0.1
EX. 17	EF-F (15)	F/H[1.5/8] (0.8) ZA	<0.1
COMP. EX. 6	EF-F (15)	H (0.8)	0.8
COMP. EX. 7	EF-F (15)	NONE	1.0

TABLE 3

	BASE MATERIAL (THICKNESS μm)	INORGANIC SUBSTANCE- CONTAINING LAYER [VOLUME RATIO] (THICKNESS μm)	OXYGEN PERMEABILITY (30° C., 60% RH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$
EX. 19	KOP (15)	F/H[3/7] (0.5)	<0.1
EX. 20	KOP (25)	F/H[3/7] (0.5)	<6.1
EX. 21	KOP (25)	F/H[4/6] (0.5)	<0.1
EX. 22	KOP (25)	F/H[2/8] (0.8)	<0.1
EX. 23	KOP (25)	F/H[1.5/8] (0.8)	<0.1
EX. 24	KOP (25)	F/H[1/8] (1.5)	<0.1
EX. 25	KET (15)	F/H[2/8] (0.8) Z	<0.1
EX. 26	KET (15)	F/H[1.5/8] (0.8) ZA	<0.1
COMP. EX. 9	KOP (15)	H (0.8)	3.0
COMP. EX. 10	KOP (15)	NONE	8.5

We claim:

1. A laminate comprising:

- (a) a layer comprising a substance having a gas barrier property; and
- (b) at least one layer which is disposed on the layer (a) wherein said layer (b) comprises a resin composition comprising a resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000, said inorganic laminar compound being such that it is swollen or cleft in a solvent, said inorganic laminar compound being selected from the group consisting of a graphite, a phosphoric acid salt derivative compound, a chalcogen compound, a kaolin-ite series clay mineral, an antigorite series clay mineral, a smectite series clay mineral, and a mica series clay mineral, said resin comprising one selected from the group consisting of polyvinyl alcohol (PVA), ethyl-enevinylalcohol copolymer (EVOH), polyacrylonitrile (PAN), polysaccharide, polyacrylic acid, and esters thereof.

2. A laminate according to claim 1, wherein the layer (a) comprising the gas barrier substance is disposed on another resin layer underlying the layer (a) substance.

3. A laminate according to claim 1, wherein the gas barrier substance comprises a metal or metal oxide.

4. A laminate according to claim 1, wherein the layer comprising the gas barrier substance comprises a layer comprising an ethylene-vinyl alcohol copolymer as a main component.

5. A laminate according to claim 1, wherein the layer comprising the gas barrier substance comprises a layer comprising a polyvinylidene chloride as a main component.

6. A laminate according to claim 1, wherein the inorganic laminar compound is an inorganic laminar compound having a particle size of 5 μm or smaller.

7. A laminate according to claim 1, wherein the inorganic laminar compound comprises a clay mineral having a swelling property.

8. A laminate according to claim 1, wherein the inorganic laminar compound is an inorganic laminar compound having an aspect ratio of 200 to 3000.

9. A laminate according to claim 1, wherein the inorganic laminar compound and the resin constituting the resin composition have a volume ratio (inorganic laminar compound/resin) in the range of (5/95) to (90/10).

10. A laminate according to claim 1, wherein the resin constituting the resin composition is a highly hydrogen-bonding resin.

11. A laminate according to claim 10, wherein the highly hydrogen-bonding resin is a resin such that the wt. percent of a hydrogen-bonding group or ionic group per unit weight of the resin is not less than 30% and not more than 50%.

12. A laminate according to claim 10, wherein the highly hydrogen-bonding resin is polyvinyl alcohol or polysaccharide.

13. A laminate according to claim 10, wherein the resin composition further comprises a crosslinking agent for hydrogen-bonding group.

14. A laminate according to claim 13, wherein the crosslinking agent for hydrogen-bonding group is a zirconia compound.

15. A laminate according to claim 1, which has an oxygen permeability of not more than 0.2 cc/m²·day·atm under the conditions of 30° C. and 60% RH.

16. A laminate according to claim 1, which has a shape in the form of a laminate film.

17. A laminate film, comprising: a base material, and at least one layer disposed thereon comprising a laminate according to claim 1.

18. A laminate film according to claim 17, which has an oxygen permeability of not more than 0.2 cc/m²·day·atm under the conditions of 30° C. and 60% RH.

19. A shaped article, comprising a laminate according to claim 1 as at least a portion thereof.

20. A shaped article according to claim 19, which has an oxygen permeability of not more than 0.2 cc/m²·day·atm under the conditions of 30° C. and 60% RH.

21. A laminate, comprising:

at least one layer comprising a resin selected from biaxially oriented polypropylene, biaxially oriented nylon and biaxially oriented polyethylene terephthalate; and at least one layer comprising a laminate according to claim 1.

22. A laminate according to claim 21, which has a shape in the form of a laminate film.

23. A laminate according to claim 1, wherein the inorganic laminar compound is at least one selected from the group consisting of a graphite, a phosphoric acid salt derivative compound and a chalcogen compound.

24. A laminate according to claim 23, wherein the inorganic laminar compound is a chalcogen compound represented by the formula MX_2 , wherein M denotes an element selected from the group consisting of Group IV, Group V and Group VI, and X is S, Se, Te.

25. A laminate according to claim 24, wherein said chalcogen compound M is at least one member selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Mo and W.

26. A laminate according to claim 1, wherein the inorganic laminar compound is at least one selected from the group consisting of a salt, a kaolinite series clay mineral, antigorite series clay mineral, smectite series clay mineral, and mica series clay minerals, said inorganic compound being at least one of (i) a clay having a two-layer structure, which comprises a silica tetrahedral layer, and an octahedral layer disposed thereon and comprising a central metal; or a three-layer structure, which comprises an octahedral layer comprising a central metal, and a silica tetrahedral layer disposed on the both sides of the octahedral layer so as to sandwich the octahedral layer.

27. A laminate according to claim 26, wherein the clay mineral comprises at least one selected from the group consisting of: kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetrasilylic mica, sodium taeniolite, muscovite, margarite, talc, phlogopite, xanthophyllite, and chlorite.

* * * * *



US006146750A

United States Patent [19]

Kotani et al.

[11] **Patent Number:** 6,146,750[45] **Date of Patent:** *Nov. 14, 2000[54] **BIO-DEGRADABLE RESIN COMPOSITION,
FILM AND SHAPED ARTICLE**[75] **Inventors:** Kozo Kotani, Toyonaka; Toshio
Kawakita, Funabashi; Taiichi Sakaya;
Toshiya Kuroda, both of Takatsuki, all
of Japan[73] **Assignee:** Sumitomo Chemical Co., Ltd., Osaka,
Japan[*] **Notice:** This patent issued on a continued pro-
secution application filed under 37 CFR
1.53(d), and is subject to the twenty year
patent term provisions of 35 U.S.C.
154(a)(2).[21] **Appl. No.:** 08/522,423[22] **PCT Filed:** Jan. 24, 1995[86] **PCT No.:** PCT/JP95/00071

§ 371 Date: Sep. 22, 1995

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[87] **PCT Pub. No.:** WO95/20013

PCT Pub. Date: Jul. 27, 1995

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.⁷** B32B 5/16[52] **U.S. Cl.** 428/323; 428/324; 428/480;
428/483; 428/522; 428/532; 428/35.4; 428/36.7[58] **Field of Search** 106/607, DIG. 4;
525/56; 428/480, 483, 481, 36.7, 35.7, 35.4,
454, 522, 514, 694 BA, 324, 323, 532[56] **References Cited****U.S. PATENT DOCUMENTS**

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No. 58164.*Primary Examiner*—Paul Thibodeau*Assistant Examiner*—D. Lawrence Tarazano*Attorney, Agent, or Firm*—Pillsbury Madison & Sutro LLP[57] **ABSTRACT**

The disclosed composition contains a biodegradable resin, and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000. A biodegradable film or shaped article includes, as at least a portion thereof, a layer (1) found from this biodegradable resin composition. The biodegradable resin composition, film or shaped article can exhibit a good gas barrier property while substantially retaining the desired biodegradability. Therefore, it can considerably contribute to the maintenance or protection of a terrestrial environment such as the disposal of trash or rubbish, or plastic wastes; and the reduction in the amount of wastes in landfills.

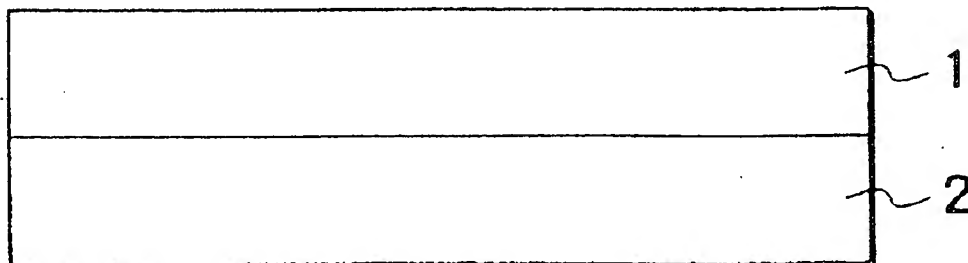
10 Claims, 9 Drawing Sheets

Fig. 1

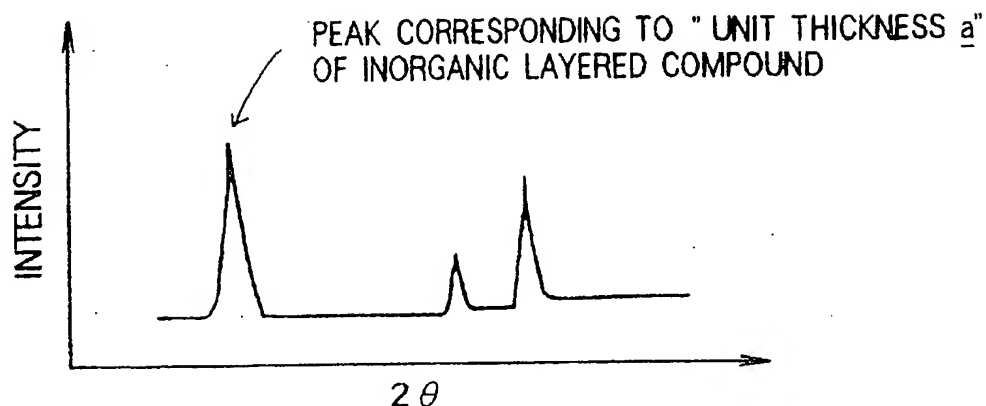
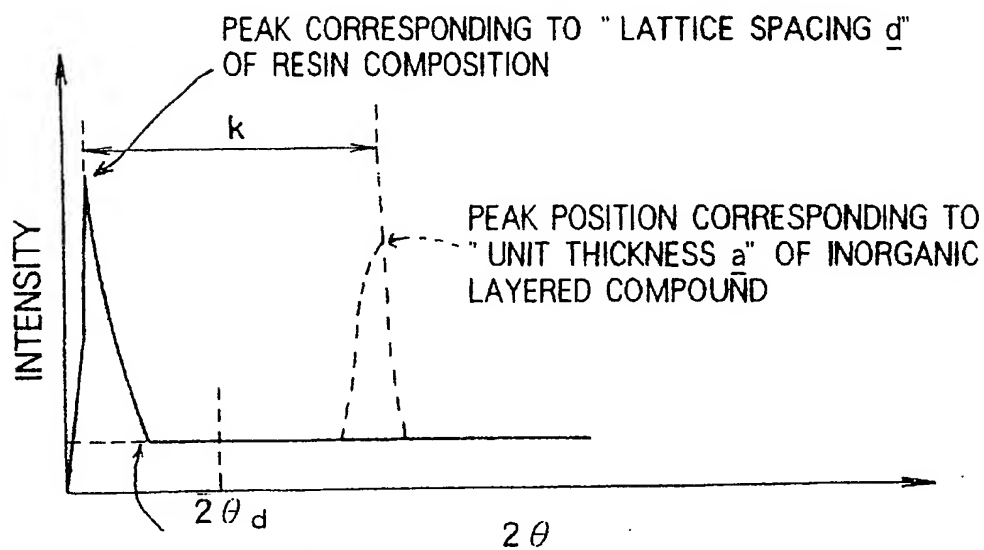


Fig. 2



BASE LINE

"k" (IN TERMS OF LENGTH) IS NOT SMALLER THAN WIDTH OF ONE RESIN CHAIN

θ_d → ANGLE OF DIFFRACTION CORRESPONDING TO ("UNIT THICKNESS \underline{a} + WIDTH OF ONE RESIN CHAIN")

Fig. 3

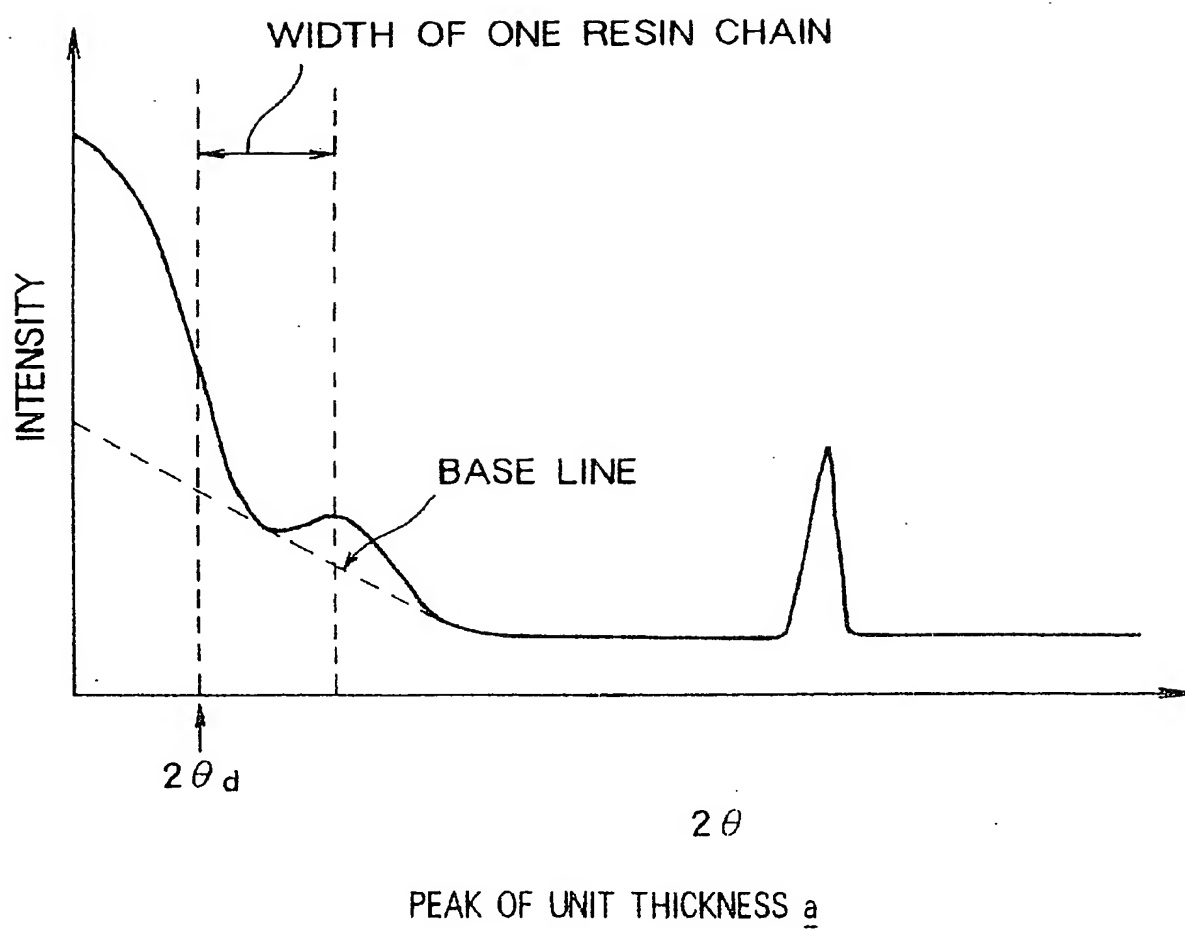


Fig. 4



Fig. 5

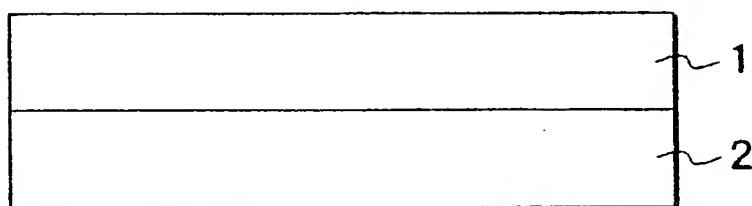


Fig. 6

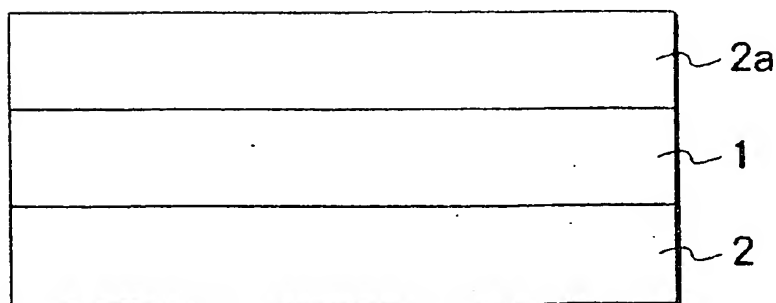


Fig. 7

TABLE 1

	BASE MATERIAL LAYER (THICKNESS μm)	INORGANIC SUBSTANCE— CONTAINING LAYER [VOLUME RATIO] (THICKNESS μm)	OXYGEN PERMEABILITY (30°C, 60%RH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$	BIO-DEGRADABILITY TEST	
				RATIO OF REMAINING AREA	APPEARANCE
EX. 1	PHB (150)	F/H [3/7] (0.5)	< 0.1	55	×
EX. 2	HBHV4 (150)	F/H [3/7] (0.5)	< 0.1	78	×
EX. 3	HBHV9 (150)	F/H [3/7] (0.5)	< 0.1	75	×
EX. 4	HBHV9 (150)	F/H [4/6] (0.8)	< 0.1	70	×
EX. 5	HBHV4 (150)	F/H [2/8] (1.5)	< 0.1	69	×
EX. 6	HBHV4 (150)	F/H [1.5/8] (2.0)	< 0.1	81	×
EX. 7	HBHV4 (150)	F/H [1/8] (1.5)	< 0.1	75	×
EX. 8	CHI (50)	F/H [2/8] (1.5)	< 0.1	51	×
EX. 9	CHIT (50)	F/H [1.5/8] (2.0)	< 0.1	40	×
EX. 10	PUR (20)	F/H [1.5/8] (2.0)	< 0.1	40	×
EX. 11	PHB (150)	F/H [2/8] (0.5) Z	< 0.1	70	×
EX. 12	PHB (150)	F/H [1.5/8] (0.8) Z	< 0.1	75	×
COMP. EX. 1	PHB (150)	NONE	50	76	×
COMP. EX. 2	HBHV4 (150)	NONE	80	DECOMPOSITION	× ×
COMP. EX. 3	HBHV9 (150)	NONE	80	30	×
COMP. EX. 4	PHB (150)	117H (0.5)	4.0	83	×
COMP. EX. 5	LDPE (60)	NONE	≥ 500	100	○

Fig. 8

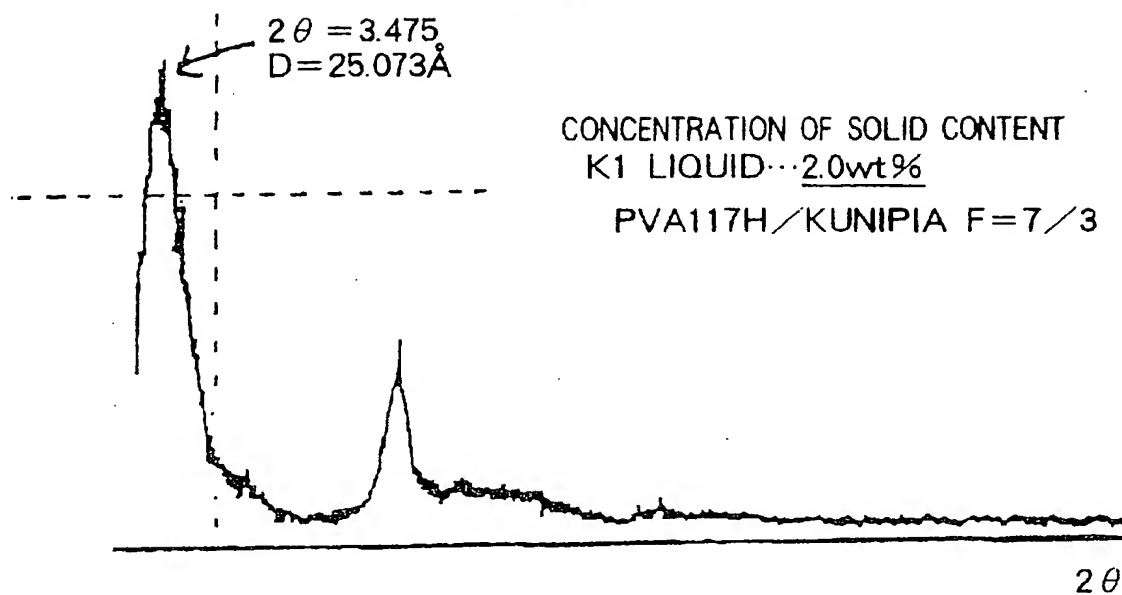


Fig. 9

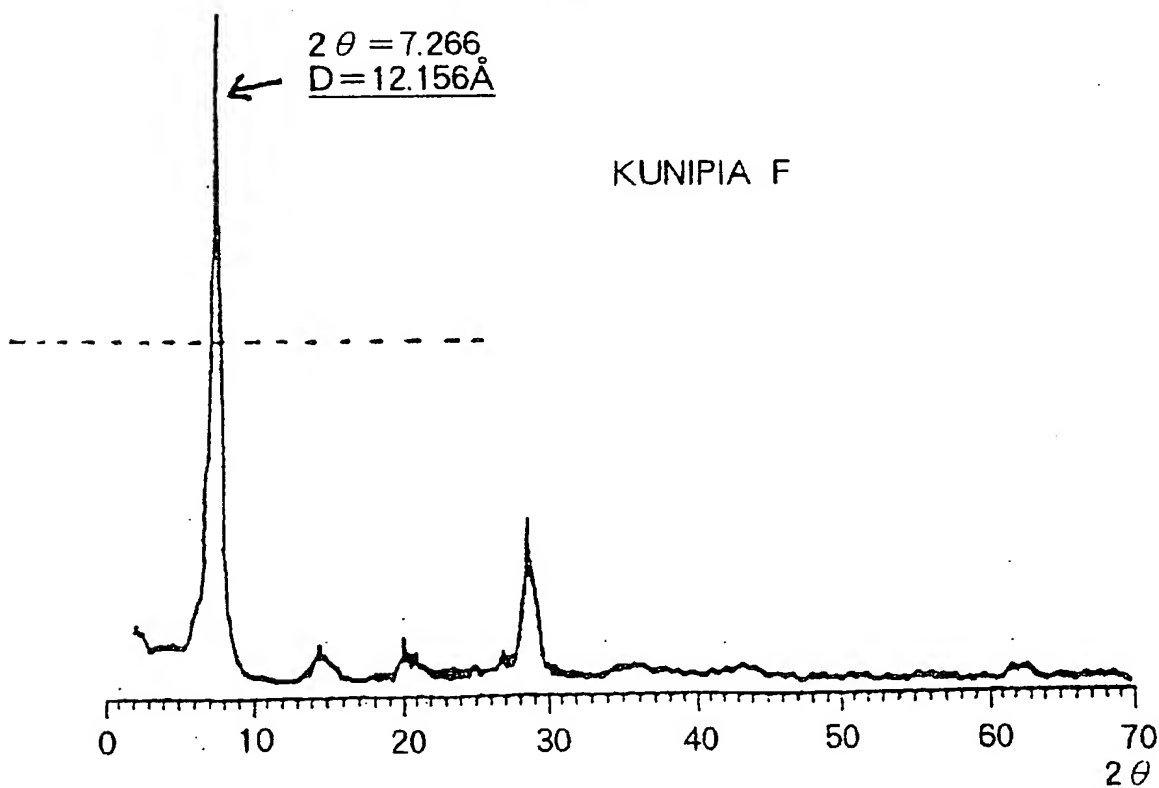


Fig. 10

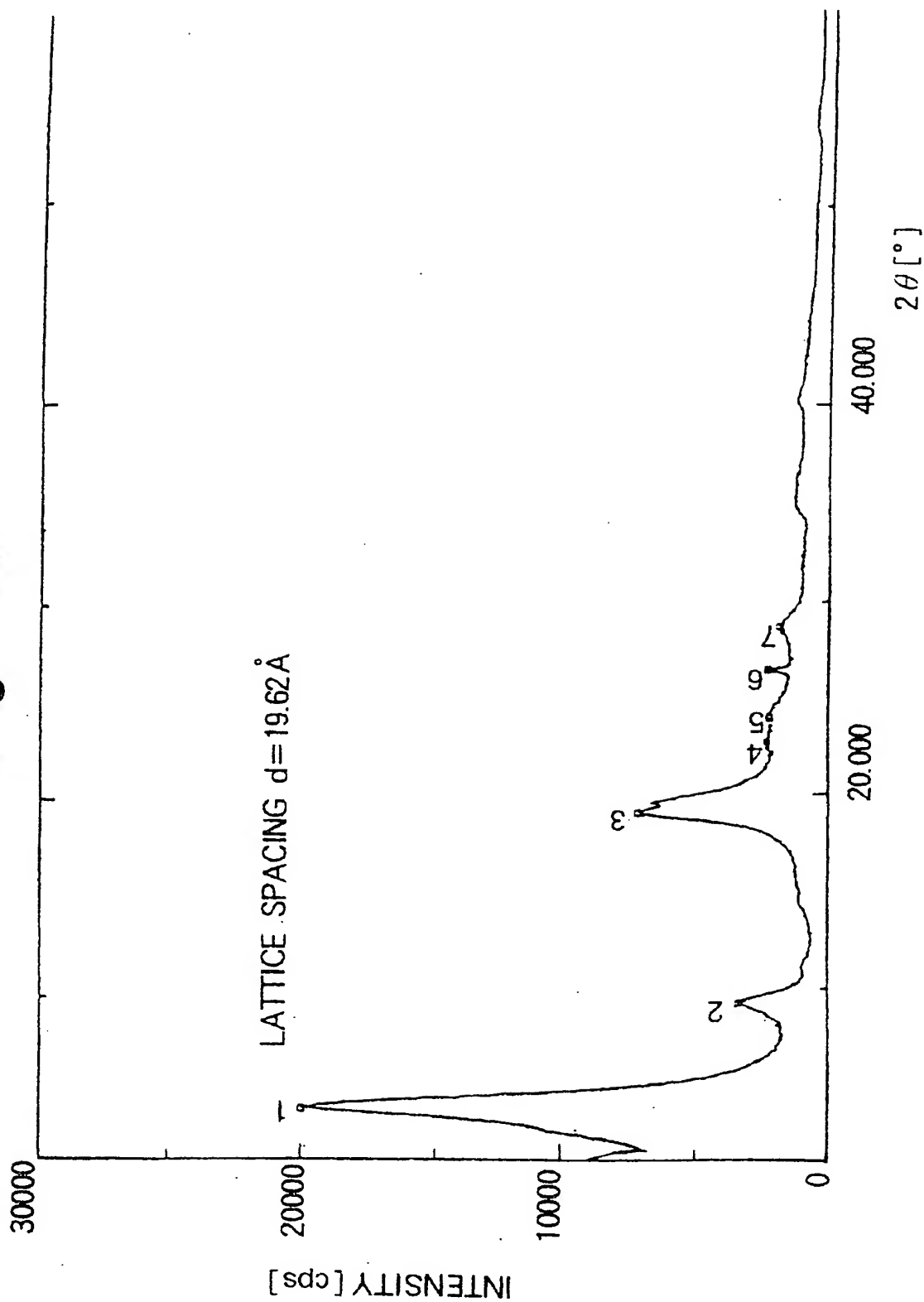


Fig. 11

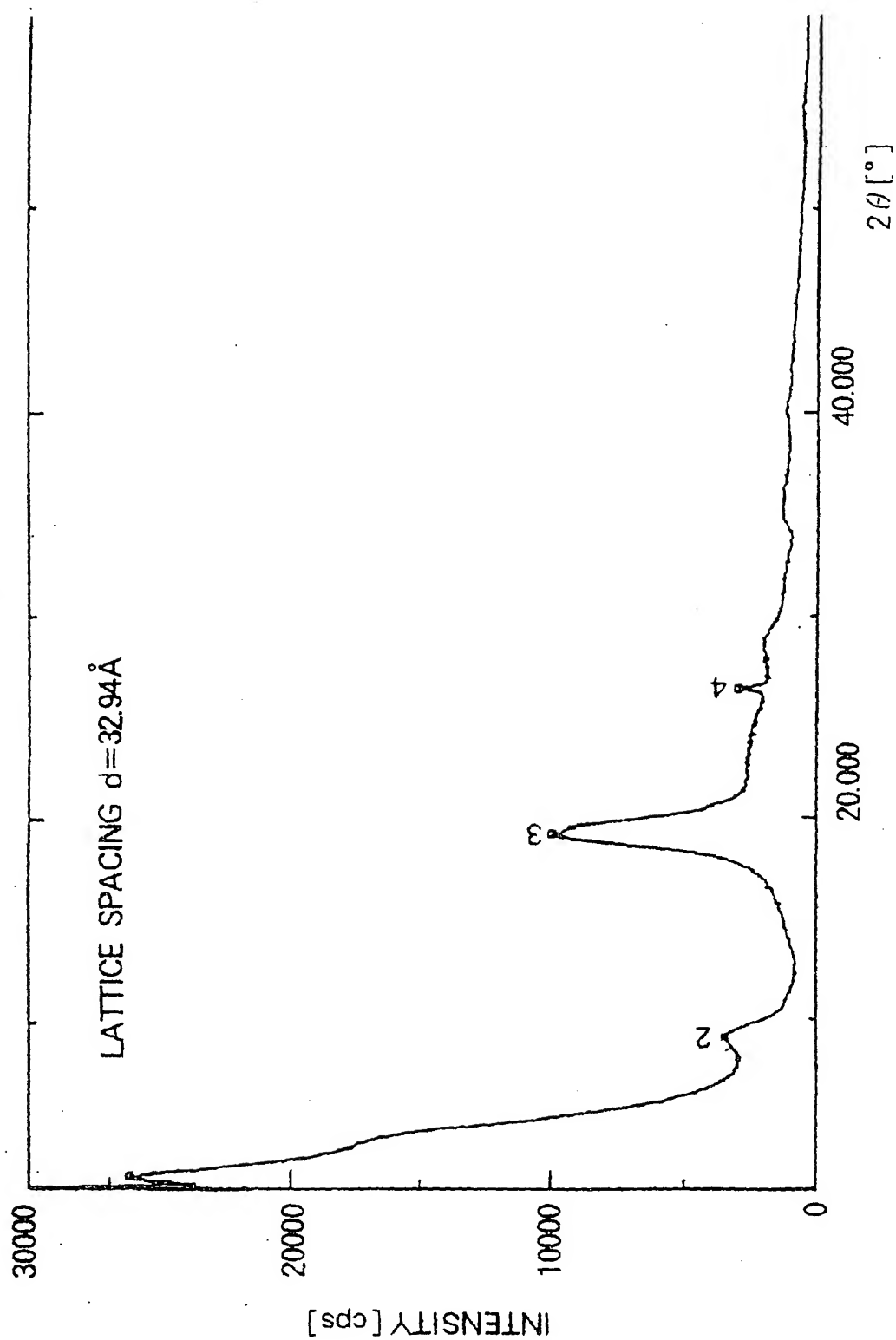


Fig. 12

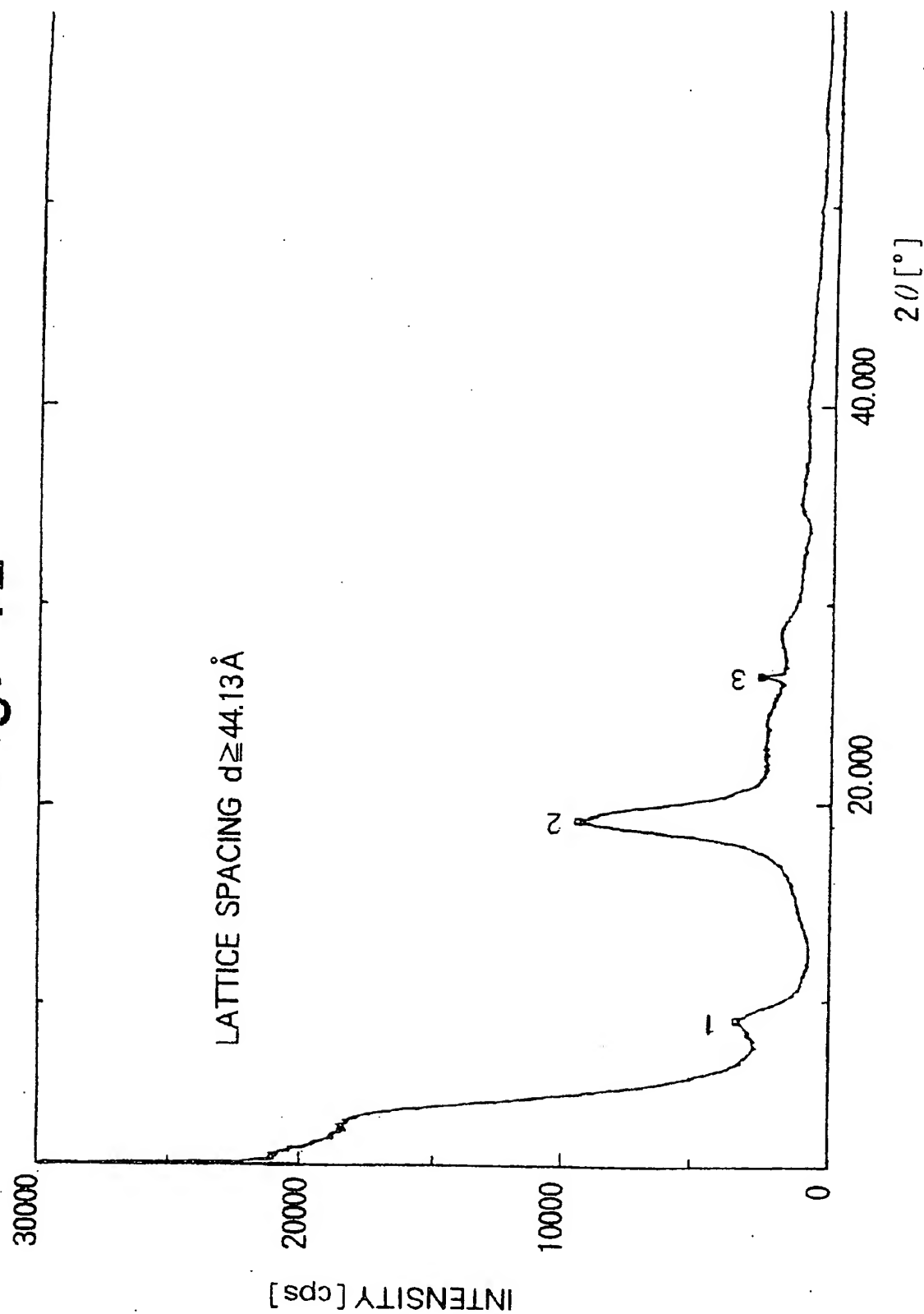
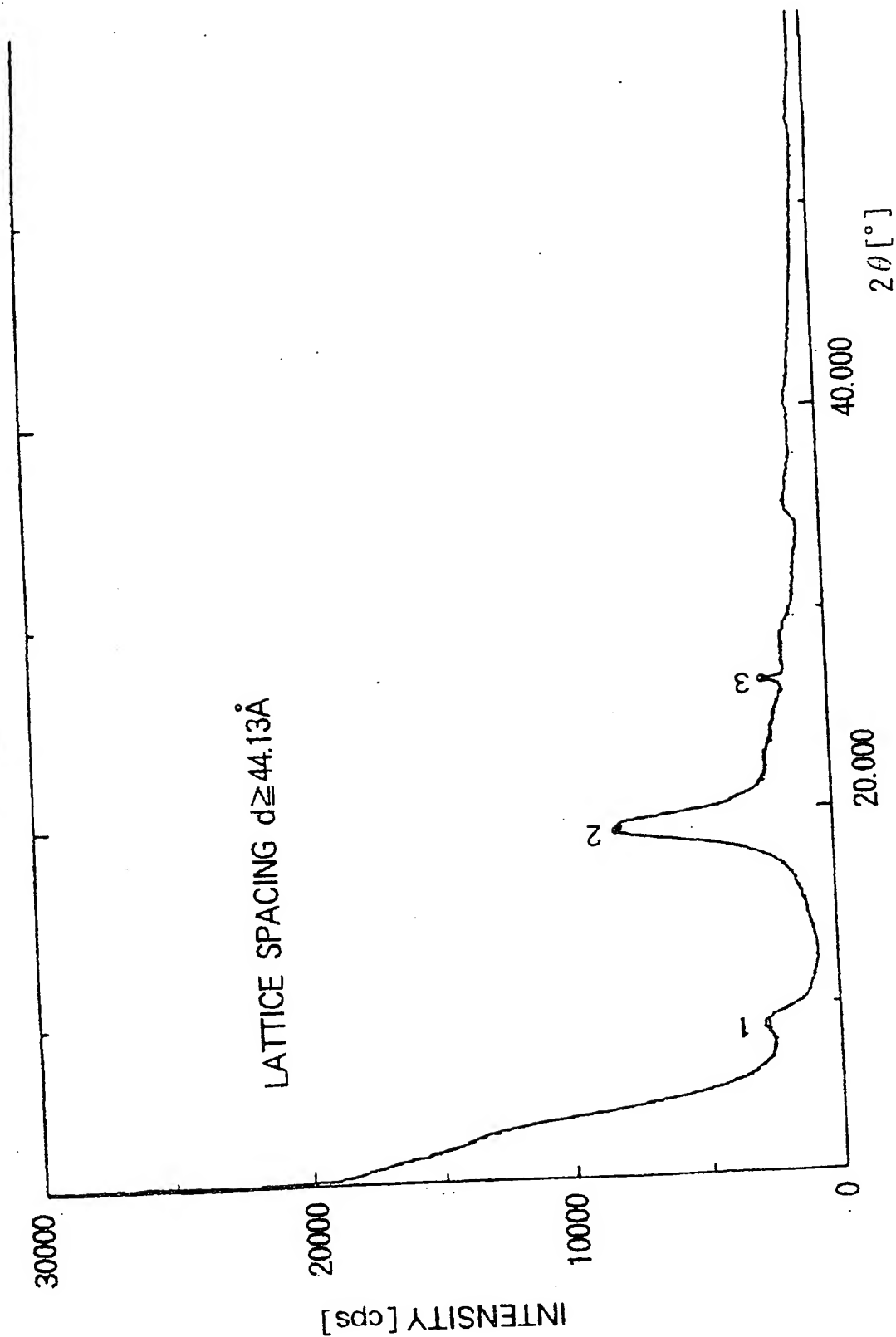


Fig. 13



BIO-DEGRADABLE RESIN COMPOSITION, FILM AND SHAPED ARTICLE

This application claims benefit of international application PCT/JP95/00071, filed Jan. 24, 1995.

BACKGROUND OF THE INVENTION

1. Technical Field

The present invention relates to a resin composition having excellent biodegradability and excellent gas barrier properties, and a film or a shaped (or molded) article comprising such a resin composition.

2. Background Art

A film having a gas barrier property (gas barrier film) is a kind of functional film that has been widely used in the fields of food, medicine, agricultural chemicals, cosmetics, etc., wherein contents to be contained therein are stored or protected while the "quality" of the contents is liable to cause a problem. One of such important use of the film includes the field of "packaging".

Packaging includes making or putting an object into a package or wrap. The material for the packaging is desired to have a wide variety of functions. For example, packaging may serve various functions including providing mechanical protection, safety, sanitary protection, workability, adaptability to goods (transparency, printability, heat sealing property), utility, profitability, etc. Having a "gas barrier property" against various gases is important as it affects the storability of the packaged contents such as food. Along with recent diversification in the form of goods distribution, in packaging techniques, and an intensification of additive control, change in taste, etc., the gas barrier property has become increasingly more important. On the other hand, the gas barrier property has heretofore been a serious weak point of ordinary plastic materials.

Factors which can deteriorate a food include oxygen, light, heat and/or moisture. Among these factors, oxygen has been considered to be a substance causing such deterioration. A material having a gas barrier property (gas barrier material) is a material which has a main function of effectively intercepting oxygen. Such a gas barrier material exhibits the function of intercepting oxygen, and simultaneously exhibits a function which is essential for various measures for controlling the deterioration of food (such as gas charging and vacuum packaging). The gas barrier material has been utilized very effectively in many fields such as food packaging inclusive of confectionery bags, bags for dried bonito, pouches for retorted foods, containers for carbonated drinks, etc., or packaging for cosmetics, agricultural chemicals, and medical use, on the basis of its barrier function to various kinds of gases such as oxygen, organic solvent vapors, aromas; or on the basis of its function of preventing corrosion, odor, sublimation, etc., based on the barrier function thereof.

Among films comprised of a thermoplastic resin, those films comprising oriented polypropylene, polyester, polyamide, etc., particularly have excellent mechanical, heat resistance, and transparency properties, etc., and therefore these films are widely used as a packaging material. However, the barrier property against oxygen permeability is insufficient as these films have large gas permeability. Therefore, in a case where a film comprised of such a material is used for food packaging, the food in the package is liable to be deteriorated due to degradation based on oxidation, or the function of aerobic bacteria, etc. Accordingly, when a film of the above-mentioned material

such as polypropylene is used for food packaging, it is usual to adopt a method wherein another film (or layer) having an excellent oxygen barrier property is laminated onto the film of the above-mentioned material.

The following two methods are representative measures for forming such a film having a good barrier property to oxygen. One method involves using a metal foil lamination such as aluminum foil lamination. The other method involves vapor-depositing a metal onto a surface of a thermoplastic resin film. In these methods, the excellent gas barrier property (particularly, a gas barrier permeability to oxygen) of the resultant metal foil has been effectively utilized.

On the other hand, as a transparent plastic raw material having a small oxygen permeability, there have heretofore been known some films comprising a raw material such as polyvinyl alcohol, polyethylene-vinyl alcohol copolymer, and polyvinylidene chloride-type resin. However, these plastic materials have an oxygen permeability to a certain degree which is never negligible, while a metal or glass raw material to be used for canned foods or bottled foods only has a substantially no oxygen permeability.

Methods involving dispersing an inorganic substance (in a flat shape) in a resin are known techniques for imparting gas barrier properties or increasing the gas barrier property of a resin. For example, Japanese Laid-Open Patent Application (KOKAI) No. 148532/1987 (i.e., Sho 62-148532) describes a process for producing a film having a gas barrier property wherein a coating liquid composition comprising a transparent thermoplastic resin and mica in the form of flakes having a particle size of 500 μm or smaller and an aspect ratio of 5 or larger, is applied onto a base material having a releasing property and then dried, and thereafter is peeled from the base material.

In addition, Japanese Laid-Open Patent Application No. 043554/1989 (i.e., Sho 64-043554) discloses a resin composition for barrier layer wherein muscovite ($\text{KAl}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$; non-swelling type mica) is used as mica in the form of flakes, the particle size is made smaller than 325 mesh (44 μm), and the aspect ratio is in the range of 20–140. Further, Japanese Laid-Open Patent Application No. 093542/1991 (i.e., Hei 03-093542) discloses a process for producing a plastic film having a barrier property wherein a coating composition comprising a silyl group-containing modified polyvinyl alcohol and synthetic hectorite (trade name: Laponite XLS, mfd. by Nihon Silica Kogyo Co.) in a wt. ratio of 50:50, is applied onto a biaxially oriented polyethylene terephthalate (OPET), and then subjected to drying and heat treatment (130° C. to 150° C.).

In general, the above-mentioned packaging material is used for a "disposable or throwaway" application. Therefore, it is important to impart a biodegradability to the packaging material, as some problems in the terrestrial environment have attracted more and more attention in recent years.

However, at present, a material which has a high gas barrier property to an extent such that it is suitable for the preservation and/or protection of a content to be contained in the material, and also has a biodegradability to an extent such that it can contribute to the maintenance or protection of the terrestrial environment has not yet been on the market.

SUMMARY AND OBJECTS OF THE INVENTION

An object of the present invention is to provide a resin composition, a film, or a shaped article which solves the above-mentioned problems.

A more specific object of the present invention is to provide a resin composition, a film, or a shaped article having both biodegradability as well as an oxygen barrier properties at a good level.

As a result of earnest study, the present inventors have found that a resin composition having an excellent biodegradability as well as an excellent gas barrier property has been provided by constituting a resin composition while an inorganic laminar compound having a specific aspect ratio is combined with a biodegradable resin. As a result of further study, the present inventors have also found that the above-mentioned excellent biodegradability and gas barrier properties are substantially retained, even when a biodegradable resin film or shaped article is constituted by incorporating thereinto at least a layer (or portion) comprising the above-mentioned specific resin composition.

The biodegradable resin composition according to the present invention is based on the above discovery and comprises: a biodegradable resin; and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000.

The present invention also provides a biodegradable resin film or shaped article comprising, as at least a layer (or portion) thereof, a biodegradable resin composition which comprises: a biodegradable resin; and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph schematically showing a relationship between an X-ray diffraction peak of an inorganic laminar compound and a "unit thickness a " of the compound.

FIG. 2 is a graph schematically showing a relationship between an X-ray diffraction peak of a resin composition containing an inorganic laminar compound and a "lattice spacing (or distance between lattice planes) d " of the composition.

FIG. 3 is a graph schematically showing a relationship between an X-ray diffraction peak of a resin composition and a "lattice spacing d " of the composition, in a case where the peak corresponding to the lattice spacing d is superposed on halo (or background) and is difficult to be detected. In this Figure, the area obtained by subtracting a "base line" portion from the peak area in the lower angle side below $2\theta_d$ is treated as the peak corresponding to the "lattice spacing d ".

FIG. 4 is a schematic sectional view showing an embodiment of the biodegradable resin film according to the present invention.

FIG. 5 is a schematic sectional view showing another embodiment (laminar type) of the biodegradable resin film according to the present invention.

FIG. 6 is a schematic sectional view showing a further embodiment (laminar type) of the biodegradable resin film according to the present invention.

FIG. 7 (Table 1) is a table showing the structure of laminate films and the data of oxygen permeability, etc., obtained in Examples appearing hereinafter.

FIG. 8 is a graph showing X-ray diffraction peaks of a composition comprising a polyvinyl alcohol PVA-117H and "Kunipia F" used in Examples.

FIG. 9 is a graph showing X-ray diffraction peaks of "Kunipia F" (montmorillonite) used in Examples.

FIG. 10 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d=19.62$ angstrom (pattern of the above FIG. 2).

FIG. 11 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d=32.94$ angstrom (pattern including the above patterns of FIGS. 2 and 3).

FIG. 12 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d\geq 44.13$ angstrom (pattern of the above FIG. 3).

FIG. 13 is a graph showing X-ray diffraction peaks of a composition having a lattice spacing $d\geq 44.13$ angstrom (pattern of the above FIG. 3).

DETAILED DESCRIPTION OF THE INVENTION

The present invention is now described with reference to the accompanying drawings, as appropriate.

A resin which is biodegradable (or bio-disintegrable) can be used, without particular limitation, as the biodegradable resin composition in the present composition. The expressions "biodegradable" or "biodisintegrable resin" as used herein refers to a resin having such a property that it is capable of being degraded (or broken-down) or disintegrated under the action of a microorganism.

The biodegradable resin composition, film and shaped article according to the present invention may preferably have a biodegradability which is equal to or comparable to a representative commercially available biodegradable resin, "Biopol" (trade name; poly-3-hydroxybutyrate, mfd. by ICI, United Kingdom).

More specifically, e.g., when a biodegradable resin composition is formed into a film shape having a thickness of about $150\text{ }\mu\text{m}$ and then subjected to the following biodegradability test, a sample comprising the biodegradable resin composition according to the present invention may preferably have a residual area ratio S satisfying a relationship of $\leq 0\text{ } S < 90$. Herein, "B" denotes the residual area ratio of the above-mentioned "Biopol" (poly-3-hydroxybutyrate) as a comparative sample, and "S" denotes the residual area ratio of a sample comprising the biodegradable resin composition according to the present invention. Further, a sample comprising the biodegradable resin composition according to the present invention may preferably have a "relative" residual area ratio (%) of 130% or less (more preferably, 100% or less, particularly preferably, 80% or less), provided that the "relative" residual area ratio (%) = $(S/B) \times 100$. The "residual area ratio" = (base area of film after the degradation test) / (base area of film before the degradation test) $\times 100$.

Biodegradability Test

There is provided a "Poly-Cup" (a wide-mouthed bottle-type container made of polyethylene) having a capacity of 1000 mL, with four openings (each of 1 cm square) provided to the bottom thereof so that the resultant four openings are arranged in a square-like configuration with a distance therebetween of about 15 mm counted from each other. Into the Poly-Cup, there is charged about 500 mL of culture soil (trade name: "Kumiai-Taihei Horticultural Soil", mfd. by Taihei Bussan Co.) containing 0.35 g/l kg (per culture soil) of nitrogen, 1.5 g/l kg of phosphoric acid, and 0.35 g/l kg of potassium, and having a pH of 6.0–5.5. Onto the surface of the thus charged culture soil, three pieces of sample films (wherein two pieces of the sample films comprise a resin composition to be evaluated, and the other one piece of the sample film comprises the above-mentioned "Biopol" as a standard sample) having a film thickness of about $150\text{ }\mu\text{m}$, and a base area of about 28.4 cm^2 are disposed so that the three sample films are not overlapped to each other. The thus disposed films are further covered with the above-mentioned

culture soil so that the above-mentioned 1000 mL Poly-Cup is filled up with the soil.

The resultant Poly-Cup is placed on a predetermined open-air ground (average temperature: about 25 ° C.) and is left standing with the elapse of time, while providing water in an amount of about 200 mL per one Poly-Cup with a frequency of once per three days so as to always maintain the culture soil contained in the Poly-Cup in a wet state. In the states of the films after a period of two months counted from the beginning of the test, the appearances and residual area (ratios) of the above three films are observed.

As the above biodegradable resin, it is preferred to use a biopolymer which is capable of being synthesized in a living organism (and a chemically modified product thereof), or a synthetic biodegradable polymer. More specific examples of such a polymer may include: for example, cellulose; cellulose derivatives such as hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose; polysaccharides and chemically modified product thereof such as amylose, amylopectin, pullulan, curdlan, xanthan, chitin, and chitosan; polyesters producible by microorganisms such as poly-3-hydroxybutyrate, and 3-hydroxybutyrate-3-hydroxyvalerate copolymer; and enzymatically degradable synthetic polymers, such as biodegradable aliphatic polyesters, polyvinyl alcohol, and polyethylene glycol.

Highly-hydrogen-bonding Resin

The biodegradable resin usable in the present invention may preferably be a highly hydrogen-bonding resin, in view of the gas barrier property thereof. The "highly hydrogen-bonding resin" may preferably be a resin having a weight percent (percent by weight) of a hydrogen-bonding group (in a case where the resin contains two or more of the hydrogen-bonding groups, total of these groups) per unit weight of the resin, which is 10% or more, more preferably about 20%–60%.

The "hydrogen-bonding group" used herein refers to a group having at least one hydrogen atom directly bonded to a hetero atom (i.e., atom other than carbon). Specific examples of the hydrogen-bonding group may include: hydroxyl group (inclusive of carboxyl group), amino group, thiol group, amide group, etc.

The content of the hydrogen-bonding group or ionic group may preferably be measured, e.g., by utilizing a technique of nuclear magnetic resonance (NMR), such as ¹H-NMR and ¹³C-NMR.

The highly hydrogen-bonding resin useful in the present invention is not particularly limited, as long as it has a highly hydrogen-bonding property as described above. Preferred examples of the highly hydrogen-bonding resin may include: polyvinyl alcohol, polysaccharide, derivatives of these resins, etc. In the case of an ideal polyvinyl alcohol, i.e., $-(CH_2CHOH)_n-$, the weight percent of the OH group as the above-mentioned hydrogen-bonding group is $(17/44) \times 100 = \text{about } 39\%$.

In the present invention, the "polyvinyl alcohol" refers to a polymer predominantly comprising a monomer unit of vinyl alcohol. Specific examples of such a "polyvinyl alcohol" may include: a polymer (exactly, a copolymer of vinyl alcohol and vinyl acetate) obtained by subjecting the acetic acid portion of a vinyl acetate polymer to hydrolysis or ester interchange (saponification), and polymers obtained by saponifying a polymer such as vinyl trifluoroacetate polymer, vinyl formate polymer, vinyl pivalate polymer, t-butyl vinyl ether polymer, and trimethylsilyl vinyl ether polymer. A person skilled in the art can refer to a book entitled "PVA no Sekai (World of PVA)" edited by POVAL-KAI (POVAL Society), (1992), published by KOBUNSI

KANKO-KAI (Polymer Publishing Society) K. K.; and a book entitled "Poal" written by Nagano et al. (1981), published by KOBUNSI KANKO-KAI for details about the polyvinyl alcohol.

The degree of the "saponification" in the polyvinyl alcohol may preferably be not less than 70%, more preferably, not less than 85%, in terms of mole percentage. The degree of polymerization of the polyvinyl alcohol may preferably be not less than 100 and not more than 5000 (more preferably, not less than 200 and not more than 3000).

On the other hand, "polysaccharide and derivatives thereof" usable in the present invention may also include biopolymers which are synthesized in a living organism on the basis of condensation polymerization, and those obtained by chemically modifying these biopolymers. Specific examples of the "polysaccharide and derivatives thereof" may include: cellulose, cellulose derivatives such as hydroxymethyl cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose; amylose, amylopectin, pullulan, curdlan, xanthan, chitin, chitosan, etc.

Inorganic Laminar Compound

The "layered compound" refers to a compound or substance having a layer structure. The "layer structure" is a structure wherein planes, each of which comprises atoms strongly bonded to each other on the basis of covalent bonds, etc., so as to form close packing, are stacked substantially parallel to each other on the basis of weak bonding power such as Van der Waals force.

The "inorganic laminar compound" usable in the present invention is not particularly limited, as long as the "aspect ratio" thereof measured by a method described hereinafter is not less than 50 and not more than 5000. In view of the gas barrier property, the aspect ratio may preferably be not less than 100 (particularly, not less than 200).

When the above aspect ratio is less than 50, the exhibition of the gas barrier property becomes insufficient. On the other hand, it is technically difficult to obtain an inorganic laminar compound having an aspect ratio exceeding 5000, and further such a compound is costly or expensive from an economic viewpoint. The ease in production of an inorganic laminar compound, the aspect ratio may preferably be not more than 2000 (more preferably, not more than 1500). In view of the balance between the gas barrier property and the ease of its production, the aspect ratio may preferably be in the range of 200–3000.

In view of the film forming property or formability in the form of a film or shaped article, the "particle size" measured by a method therefor described hereinafter may preferably be not more than 5 μm. When the particle size exceeds 5 μm, the film forming property or formability of a resin composition tends to be decreased. In view of the transparency of a resin composition, the particle size may more preferably be not more than 3 μm. In a case where the resin composition according to the present invention is used for a purpose (e.g., purpose of food packaging) wherein the transparency is important, the particle size may particularly preferably be not more than 1 μm.

In view of the effect thereof on an ecological environment, the inorganic laminar compound to be used in the present invention may preferably be one which is non-poisonous or substantially non-poisonous in an ecological system. Specific examples of such an inorganic laminar compound may include: e.g., phosphoric acid salt-type derivative compounds (such as zirconium phosphate-type compound), clay-type minerals, etc.

In view of the ease in obtaining a very large aspect ratio (an aspect ratio of about 200 or more), it is preferred to use

an inorganic laminar compound having a property such that it is swollen or cleft in a solvent.

The degree of the "swelling or cleavage" of the inorganic laminar compound to be used in the present invention in a solvent may be evaluated by a "swelling or cleavage" test. The inorganic laminar compound may preferably have a swelling property of not less than about 5 (more preferably, not less than about 20) according to the following swelling test. On the other hand, the inorganic laminar compound may preferably have a cleavage property of not less than about 5 (more preferably, not less than about 20) according to the following cleavage test. In these cases, a solvent having a lower density than the density of the inorganic laminar compound is used. When the inorganic laminar compound is a natural clay mineral having a swelling property, it is preferred to use water as the above solvent.

Various methodologies for testing the properties of the laminar compound are described hereinbelow.

Swelling Property Test

2 g of an inorganic laminar compound is slowly added to 100 mL of a solvent, while 100 mL-graduated cylinder is used as a container. The resultant mixture is left standing, and thereafter the volume of the former (the dispersion layer of the inorganic laminar compound) is read from the graduation corresponding to the interface between the dispersion layer of the inorganic laminar compound and the supernatant after 24 hours at 23° C. When the resultant value is larger, the swelling property is higher.

Cleavage Property Test

30 g of an inorganic laminar compound is slowly added to 1500 mL of a solvent, and is dispersed by means of a dispersion machine (DESPER MH-L, mfd. by Asada Tekko K. K., vane diameter=52 mm, rotating speed=3100 rpm, container capacity=3 L, distance between the bottom face and the vane=28 mm) for 90 minutes at a peripheral speed of 8.5 m/sec (23° C.). Thereafter, 100 mL of the resultant dispersion liquid is taken out and placed into a graduated cylinder, and then is left standing for 60 minutes. Then, the volume of the dispersion layer of the inorganic laminar compound is read from the graduation corresponding to the interface between the dispersion layer of the inorganic laminar compound and the supernatant.

As the inorganic laminar compound capable of being swollen or cleft in a solvent, it is particularly preferred to use a clay mineral having a swelling or cleaving property. The clay minerals may be classified into two types, i.e., one type having a two-layer structure, which comprises a silica tetrahedral layer, and an octahedral layer disposed thereon and comprising a central metal such as aluminum and magnesium; and another type having a three-layer structure, which comprises an octahedral layer comprising a central metal such as aluminum and magnesium, and a silica tetrahedral layer disposed on both sides of the octahedral layer so as to sandwich the octahedral layer.

Specific examples of the former two-layer type may include: kaolinite series, antigorite series, etc. Specific examples of the latter three-layer type may include: smectite series, vermiculite series, mica series, etc., depending on an interlayer cation contained therein.

More specific examples of the clay mineral may include: kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetrasilylic mica, sodium taeniolite, muscovite, mercallite or margarosanite, talc, vermiculite, phlogopite, xanthophyllite, chlorite, etc.

Particle Size

In view of difficulty, etc., in the measurement of the (true) particle size in a resin composition, in the present invention,

a value (L) which may be determined in a solvent by a dynamic light scattering method (photon correlation spectroscopy) as described hereinafter is used as the "particle size" of the inorganic laminar compound. The "dynamic light scattering method" used herein is a particle size-measuring method utilizing a scattering phenomenon of laser light, wherein scattering light from particles conducting Brownian movement, i.e., scattering light with fluctuation depending on the moving velocity or particle size (grain size) of these particles, is detected, and an information on the particle size is obtained by calculation.

According to the present inventors' knowledge, the particle size of the inorganic laminar compound contained in a resin may be approximated by the above mentioned "particle size in a solvent" obtained by the dynamic light scattering method. For example, in a case where an inorganic laminar compound which has sufficiently been swollen with a solvent (which is the same kind of the solvent used in the dynamic light scattering method) is combined with a resin, the particle size of the inorganic laminar compound contained in the resin may sufficiently be approximated by the "particle size in a solvent" obtained by the dynamic light scattering method.

Aspect Ratio

In the present invention, the aspect ratio (Z) of the inorganic laminar compound is a ratio which may be determined on the basis of a relationship of $Z=L/a$. In this relationship, L is the particle size of an inorganic laminar compound determined by the dynamic light scattering method in a solvent, and a is the "unit thickness" of the inorganic laminar compound. The "unit thickness a" is a value which is determined on the basis of the measurement of the inorganic laminar compound alone, by a powder X-ray diffraction method, etc., as described hereinafter. More specifically, as schematically shown in the graph of FIG. 1 wherein the abscissa denotes 2θ , and the ordinate denotes the intensity of X-ray diffraction peaks, the "unit thickness a" is a spacing obtained from the Bragg's equation ($n\lambda=2\cdot D\cdot \sin \theta$, $n=1, 2, 3 \dots$), wherein θ denotes the angle corresponding to the peak having the lowermost angle among those of the observed diffraction peaks. A person skilled in the art can refer to a book entitled "Kiki-Bunseki no Tebiki (Handbook on Instrumental Analysis) (a)", page 69, (1985), editorially supervised by Jiro SHIOKAWA, published by KAGAKU DOJIN K. K. for the details of the powder X-ray diffraction method.

In correspondence to the above relationship of $Z=L/a$ based on the measurement of the inorganic laminar compound alone, when the resin composition according to the present invention is subjected to the powder X-ray diffraction method, the lattice spacing d of the inorganic laminar compound contained in the resin composition may usually be obtained.

More specifically, as schematically shown in the graph of FIG. 2 wherein the abscissa denotes 2θ , and the ordinate denotes the intensity of X-ray diffraction peaks, the "lattice spacing d" ($a < d$) is a spacing corresponding to the peak having the lowermost angle among the observed diffraction peaks appearing on the lower angle (larger spacing) side as compared with the position of the diffraction peak corresponding to the above-mentioned "unit thickness a". In a case where the above peak corresponding to the "lattice spacing d" is superposed on a halo (or background) as schematically shown in the graph of FIG. 3 so that it is difficult to detect such a peak, the area of a portion obtained by subtracting the base line portion from a portion corresponding to an angle lower than $2\theta_d$, is treated as a peak

corresponding to the "lattice spacing d ". The θ_d used herein is an angle of diffraction corresponding to "(unit length a + (width of one resin chain))". A person skilled in the art can refer to a book entitled "Nendo no Jiten (Encyclopedia of Clay)", page 35 et seq. and page 271 et seq., (1985), edited by Shuichi IWAJO et al., published by ASAKURA SHOTEN K. K. for the details of a method for determining "the lattice spacing d ."

The integrated intensity of the diffraction peak (corresponding to the "lattice spacing d ") observed in the powder X-ray diffraction of a resin composition may preferably have a relative ratio of not less than 2 (more preferably, not less than 10), with respect to the integrated intensity of the diffraction peak as a standard (corresponding to the "lattice spacing a ").

In general, the difference between the above lattice spacing d and the "unit thickness a ", namely, the value of $k=(d-a)$ (when converted into "length") may be equal to, or larger than the width of one resin chain constituting the resin composition ($k=(d-a) \geq (\text{width of one resin chain})$). The "width of one resin chain" may be determined by simulation calculation, etc. (as described in, e.g., a book entitled "KOBUNSHI KAGAKU JORON (Introduction to Polymer Chemistry)", pages 103-110 (1981), published by KAGAKU DOJIN K. K.). In the case of polyvinyl alcohol, this width is 4-5 Å (angstrom), and in the case of water molecules, this width is 2-3 Å.

It is considered that the above-mentioned aspect ratio $Z=L/a$ is not always equal to "true aspect ratio" of the inorganic laminar compound in the resin composition. However, it is reasonable to approximate the "true aspect ratio" by the aspect ratio Z , for the following reason.

It is extremely difficult to directly measure the "true aspect ratio" of the inorganic laminar compound contained in a resin composition. On the other hand, in a case where there is a relationship of $a < d$ between the lattice spacing d determined by the powder X-ray diffraction method for the resin composition, and the "unit thickness a " determined by the powder X-ray diffraction method for the inorganic laminar compound alone; and the value of $(d-a)$ is not smaller than the width of one resin chain in the resin composition, it is assumed that the resin is inserted between layers of the inorganic laminar compound. Accordingly, it is sufficiently reasonable to approximate the thickness of the inorganic laminar compound in the resin composition by the above-mentioned "unit thickness a ", i.e., to approximate the "true aspect ratio" in the resin composition by the above-mentioned "aspect ratio Z " of the inorganic laminar compound alone.

As mentioned above, it is extremely difficult to measure the true particle size in the resin composition. However, it may be considered that the particle size of the inorganic laminar compound in the resin is quite near to the particle size in a solvent, when the inorganic laminar compound, which has been fully swollen with a solvent of the same kind as that of the solvent used in the dynamic light scattering method, is combined with a resin to provide a resin composition.

However, it is hardly considered that the particle size L determined by the dynamic light scattering method exceeds the major axis length L_{max} of the inorganic laminar compound, and therefore the possibility that true aspect ratio (L_{max}/a) is smaller than the "aspect ratio Z " used in the present invention (i.e., the possibility of $L_{max}/a < Z$), is theoretically very small.

In consideration of the above-mentioned two viewpoints, it is considered that the definition of the aspect ratio Z used

in the present invention is sufficiently reasonable. Thus, in the present specification, the "aspect ratio" or "particle size" means the "aspect ratio Z " as defined above, or "particle size L " determined by the dynamic light scattering method.

5 Solvent

In the present invention, the solvent for swelling the inorganic laminar compound is not particularly limited, as long as it is usable in the production of the resin composition. For example, when a natural clay mineral having a swelling property is used as an inorganic laminar compound, specific examples of the solvent may include: water, alcohols such as methanol; polar solvent such as dimethylformamide, dimethyl sulfoxide, and acetone; or mixtures comprising two or more species selected from these solvents. It is preferred to use water or an alcohol such as methanol having a relatively low boiling point, in view of the ease in its removal after film formation or shaping of the resin composition.

Crosslinking Agent for Hydrogen-Bonding Group

In the present invention, in a case where a highly hydrogen-bonding resin is used as the biodegradable resin, a crosslinking agent for a hydrogen-bonding group may be used as desired, for the purpose of improving the water resistance (or barrier property after water-resistance environmental test) of the highly hydrogen-bonding resin.

The crosslinking agent for the hydrogen-bonding group usable in the present invention is not particularly limited. Preferred examples of the crosslinking agent may include: titanium-type coupling agent, silane-type coupling agent, melamine-type coupling agent, epoxy-type coupling agent, isocyanate-type coupling agent, copper compound, zirconia compound, etc. In view of the water resistance, a zirconia compound may particularly preferably be used.

Specific examples of the zirconia compound may include: halogenated zirconium such as zirconium oxychloride, hydroxy zirconium chloride, zirconium tetrachloride, and zirconium bromide; zirconium salts of mineral acid such as zirconium sulfate, basic zirconium sulfate, and zirconium nitrate; zirconium salts of organic acid such as zirconium formate, zirconium acetate, zirconium propionate, zirconium caprylate, and zirconium stearate; zirconium complex salts such as zirconium ammonium carbonate, zirconium sodium sulfate, zirconium ammonium acetate, zirconium sodium oxalate, zirconium sodium citrate, zirconium ammonium citrate; etc.

The amount of the addition of the crosslinking agent for a hydrogen-bonding group is not particularly limited, but the crosslinking agent may preferably be used so as to provide a ratio ($K=CN/HN$), i.e., ratio of the mole (CN) of the crosslinking-providing group of the crosslinking agent, to the mole (HN) of the hydrogen-bonding group of the highly hydrogen-bonding resin, which is not less than 0.001 and not more than 10. The above molar ratio K may more preferably be in the range of not less than 0.01 and not more than 1.

55 Transparency

A film or shaped article comprising the resin composition according to the present invention may preferably have a transparency, in view of advantage in a case where it is used for a purpose such as packaging. The transparency may preferably have a degree of not less than 80% (more preferably, not less than 85%) in terms of transmittance of whole light at a wavelength of 500 nm. For example, such a transparency may preferably be measured by means of a commercially available spectrophotometer (Automatic Recording Spectrophotometer Model-330, mfd. by Hitachi Seisakusho K. K.).

Oxygen Permeability

The resin composition, film or shaped article according to the present invention has a gas barrier property. The gas barrier property may preferably be not more than 0.5 cc/m²·day·atm, more preferably, not more than 0.2 cc/m²·day·atm (particularly preferably, not more than 0.15 cc/m²·day·atm), in terms of an oxygen permeability under the conditions of 30° C. and 60% RH (relative humidity).

Resin Composition

The method of formulating or producing the above composition comprising an inorganic laminar compound and a biodegradable resin is not particularly limited. In view of the homogeneity or ease in handling at the time of the formulation, it is possible to employ various methods. A first method involves obtaining a solution by dissolving resin, and obtaining a dispersion by preliminarily swelling or cleaving an inorganic laminar compound, and mixing these together, and thereafter removing the solvent. A second method involves adding a dispersion obtained by swelling or cleaving an inorganic laminar compound to a resin, and thereafter removing the solvent. A third method involves adding an inorganic laminar compound to a solution obtained by dissolving a resin and obtaining a dispersion in which the inorganic laminar compound is swollen or cleft, and thereafter removing the solvent. A fourth method involves kneading an inorganic laminar compound and a resin under heating, among other methods. The first, second and third methods are preferred in view of the ease of obtaining a large aspect ratio of the inorganic laminar compound.

In view of the improvement in the water resistance (barrier property after the water-resistance environmental test), it is preferred in the aforementioned first and second methods that the solvent is removed from the system and thereafter a thermal aging treatment is conducted at a temperature of not less than 110° C. and not more than 220° C. (more preferably, a temperature of not less than 130° C. and not more than 210° C.). The aging period of time is not particularly limited. In consideration of the necessity for a film temperature to reach at least a set temperature, for example, it is preferred to adopt an aging time of not less than 1 sec. and not more than 100 min. (more preferably, about 3 sec. to 10 min.) in the case of a drying method using a heating medium-contact type dryer such as hot-air dryer, in view of a balance between the water resistance and productivity.

The heat source to be used in the above aging treatment is not particularly limited. For example, it is possible to apply any of various methods such as those utilizing heat roll contact, heat medium contact (air, oil, etc.), infrared heating, and microwave heating.

The effect of improving the water resistance may remarkably be enhanced in a case where the biodegradable resin is a highly hydrogen-bonding resin, and/or the inorganic laminar compound is a clay mineral having a swelling property.

With respect to the composition ratio (volume ratio) between the inorganic laminar compound and the biodegradable resin used in the present invention, the volume ratio of inorganic laminar compound/biodegradable resin (ratio at the time of "Shikomi" (mixing for preparation)) may preferably be in the range of 5/95 to 90/10, more preferably in the range of 5/95 to 50/50 (particularly preferably, in the range of 10/90 to 30/70). A volume ratio in the range of 5/95 to 30/70 is advantageous because of the improved flexibility of the film or shaped article. In addition, a volume ratio in the range of 7/93 to 17/83 is advantageous because a decrease in the barrier property due to the folding is suppressed, and because of an increase in the peeling strength, etc.

Such a volume ratio may be determined by dividing respectively the numerator value (weight of the inorganic laminar compound) and the denominator value (weight of the biodegradable resin) constituting the weight ratio at the time of the "mixing for preparation" of these components, by respective densities. In general, there are situations in which the density of a biodegradable resin (e.g., polyvinyl alcohol) is somewhat different depending on the crystallinity thereof. However, it still is possible to calculate the volume ratio while assuming the crystallinity of the biodegradable resin to be 50%.

When the above volume ratio (volume fraction) of the above inorganic laminar compound/biodegradable resin is below 5/95, the barrier property is liable to be insufficient. On the other hand, when the above volume ratio exceeds 90/10, the resultant film forming property or formability is liable to be insufficient.

The method of formulating or producing the above composition comprising an inorganic laminar compound and a biodegradable highly hydrogen-bonding resin is not particularly limited. It is possible to use any of the following methods to produce or formulate the above composition. A first method involves dissolving a biodegradable and highly hydrogen-bonding resin, and obtaining a dispersion by preliminarily swelling or cleaving an inorganic laminar compound, mixing the foregoing with one other, and thereafter removing the solvent. A further method involves obtaining a dispersion by swelling or cleaving an inorganic laminar compound, adding it to a biodegradable and highly hydrogen-bonding resin, and thereafter removing the solvent. Yet another method involves kneading an inorganic laminar compound and a biodegradable and highly hydrogen-bonding resin together under heating conditions, among other methods. In view of easiness in the provision of a large aspect ratio of the inorganic laminar compound, it is preferred to adopt the former two methods.

Laminate Structure

The laminate structure or shaped structure of a resin composition according to the present invention is not particularly limited, as long as it comprises, as at least a portion (or layer) thereof, a biodegradable resin composition comprising a biodegradable resin and an inorganic laminar compound having an aspect ratio of not less than 50 and not more than 5000. More specifically, the resin composition according to the present invention may be shaped into any of various forms such as film, sheet, and container. However, in view of surer provision of the biodegradability of the entirety, it is preferred that a base material (i.e., the portion other than the portion or layer comprising the resin composition according to the present invention) in an embodiment wherein the resin composition according to the present invention is formed into a laminate-like shape, may also comprise a biodegradable material such as biodegradable resin, paper, and woody material.

FIG. 4 is a schematic sectional view showing an embodiment of the biodegradable resin film according to the present invention. Referring to FIG. 4, the biodegradable resin film in this embodiment comprises a layer 1 of a biodegradable resin composition containing an inorganic laminar compound.

The biodegradable resin film according to the present invention may also have a laminate structure as shown in the schematic sectional views of FIG. 5 or 6. The biodegradable resin film in the embodiment of FIG. 5 comprises a base material layer 2 comprising a biodegradable resin, and a layer 1 of a biodegradable resin composition disposed thereon containing an inorganic laminar compound. On the

other hand, the biodegradable resin film in the embodiment of FIG. 6 comprises a base material layer 2 comprising a biodegradable resin, a layer 1 of a biodegradable resin composition disposed thereon containing an inorganic laminar compound, and further a biodegradable resin layer 2a disposed on the biodegradable resin layer 1.

The method of laminating the above-mentioned resin composition according to the present invention on a base material is not particularly limited, but it is preferred to use, e.g., a coating method wherein a coating liquid is applied onto a film as a base material, and then dried and heat-treated. Specific examples of such a coating method may include: gravure methods such as direct gravure method, reverse gravure method and micro-gravure method; roll coating methods such as twin-roll bead coating method, and bottom-feed triple reverse coating method; doctor knife method, die coating method, dip coating method, bar coating method, and coating method combining these coating methods.

The thickness of a coating film (i.e., the thickness of a layer comprising a resin composition according to the present invention) may vary somewhat depending on the kind of a base material to be combined therewith, or an intended barrier performance, etc., but the thickness may preferably be not more than 10 μm in terms of the thickness after drying. In a case where a higher transparency is demanded, the thickness may preferably be not more than 2 μm (more preferably, not more than 1 μm) in terms of thickness after drying. The thickness of the coating film does not have a particular lower limit. In view of the provision of a sufficient gas barrier property, the thickness may preferably be 1 nm or, larger, more preferably 10 nm or larger (particularly preferably, 100 nm or larger).

In addition, it is possible to mix with or add to the resin composition, film or shaped article according to the present invention as desired, any of various additives such as ultraviolet light absorbing agent, colorant, and antioxidant, within a range wherein the effect of the present invention is not substantially impaired. Further, it is of course possible to use an adhesive or printing ink, as desired, e.g., at the time of laminating operation.

Hereinbelow, the present invention will be described in detail with reference to Examples, by which the present invention should not be limited.

EXAMPLES

The methods of measuring various physical properties used in the present specification are described below.

Biodegradability Test

There was provided a "Poly-Cup" having a capacity of 1000 mL, and four openings (each of 1 cm square) were provided to the bottom thereof so that the resultant four openings were arranged in a square-like configuration with a distance therebetween of about 15 mm from each other. Into the Poly-Cup, there was charged about 500 mL of culture soil (trade name: "Kumiai-Taihei Horticultural Soil", mfd. by Taihei Bussan Co.) containing 0.35 g/l kg (per culture soil) of nitrogen, 1.5 g/l kg of phosphoric acid, and 0.35 g/l kg of potassium, and having a pH of 6.0-6.5. Onto the surface of the thus charged culture soil, three pieces of sample films having a thickness of about 150 μm , and a base area of about 28.4 cm^2 were disposed so that the three sample films were not overlapped to each other. The thus disposed films were further covered with the above-mentioned culture soil so that the above-mentioned 1000 mL Poly-Cup was filled up with the soil.

The resultant Poly-Cup was placed on a predetermined place (open-air ground) and was left standing with the elapse

of time, while providing water in an amount of about 200 mL per each Poly-Cup with a frequency of once per three days so as to always maintain the culture soil contained in the Poly-Cup in a wet state. After periods of one month and two months counted from the beginning of the test, sampling of the films was respectively conducted. After two months, the degree of the degradation of the films was determined on the basis of the appearances and residual area ratios thereof.

Place: 10-1, Tsukahara 2-chome, Takatsuki-shi, Osaka-fu, Japan (an open-air ground in Sumitomo Chemical Co., Ltd.; average temperature: about 25° C.).

Period: From Jun. 4, 1993 to Aug. 9, 1993 (about two months).

After the above "biodegradability test", the ratio of the base area of the film (residual area ratio, average of the above three sample films) remaining on the culture soil was determined according to the following formula (as the residual area ratio becomes smaller, the biodegradability is better).

Residual area ratio = (base area of film after the degradation test) / (base area of film before the degradation test) \times 100.

The appearance of the film was evaluated by naked eyes according to the following standard. The meanings of the respective symbols are as follows.

o: No change was observed.

Δ : The production of pores were observed.

x: The change in the film shape was marked.

x x: The original shape of the film was reduced to pieces.

Oxygen Permeability

Oxygen permeability was measured by using a method according to Japanese Industrial Standard (JIS) (JIS K-7126).

More specifically, a sample film (test piece) was mounted to a commercially available oxygen permeability measuring apparatus (trade name: OX-TRAN 10/50A, mfd. by MOCON Co. U.S.A.), and the oxygen permeability was measured under the measuring conditions of a temperature of 31° C. (humidity-controlled thermostat=21° C.). At this time, the relative humidity was about 61%. In this measurement, the oxygen permeability of the sample film was continuously measured, and the oxygen permeability at a point of time at which the oxygen permeability became substantially constant (usually, about several hours to three days after the initiation of the measurement) was used as the data thereof in this specification. When the oxygen transmission is represented by the ordinate of a graph, and the time t is represented by the abscissa thereof, the period of time (θ sec.) wherein the film interior reaches the equilibrium may be represented by an equation of $\theta = d^2/6 \cdot D$, wherein d denotes the film thickness (μm) of the sample film, and D denotes a diffusion constant ($\mu\text{m}^2/\text{sec}$). Accordingly, the period of time for the measurement is different depending on the kind of the sample.

Thickness Measurement

A thickness of not less than 0.5 μm was measured by means of a commercially available digital-type thickness measuring device (contact-type thickness measuring device, trade name: Ultra-High Precision Deci-Micro Head MH-15M, mfd. by Nihon Kogaku Co.).

On the other hand, a thickness of less than 0.5 μm was determined by a gravimetric analysis method, wherein the weight of a film having a predetermined area was measured, the resultant weight was divided by the area, and further divided by the specific gravity of the composition; or an elemental analysis method (in the case of a laminate comprising a biodegradable resin composition layer and a base material, etc.).

In a case where the elemental analysis (measuring principle: ICP emission spectrometry, with reference to a book entitled "ICP Emission Spectrometry", edited by Nihon Bunseki Kagaku-kai (Japan Society of Analytical Chemistry), 1988, published by Kyoritsu Shuppan) was used, the ratio between the layer of the resin composition according to the present invention and the base material was determined by calculation on the basis of the ratio between the analytical value of a predetermined inorganic element (originating from the composition) of the laminate, and the fraction of a predetermined element (e.g., Si) of the inorganic laminar compound alone.

Particle Size Measurement

Predetermined parameters such as the refractive index of a solvent (e.g., $n=1.332$ in the case of water), the viscosity of the solvent (e.g., $\eta=0.890$ cP, in the case of water), and the refractive index of an inorganic laminar compound (e.g., $n=1.56$ in the case of mica) were inputted to a commercially available ultrafine particle size analyzing apparatus (trade name: BI-90, mfd. by Brookhaven Co., U.S.A., Japanese agent: Nikkiso K. K.), and measurement was conducted at a temperature of 25°C ., in a solvent of water, while a solution having a weight ratio (inorganic laminar compound/water) of 2% was diluted in accordance with an estimated particle size. Through such a method, the particle size L was determined as a central particle size value measured by a photon correlation method based on dynamic light scattering, which was automatically outputted from the above analyzer as a digital value. In this particle size measurement for the inorganic laminar compound, each time the measurement was conducted, calibration measurement was also conducted by using the following standard samples comprising true spherical fine particles, whereby it was confirmed that the measured data of the particle size of the standard samples fell within the range of relative error of $\pm 10\%$.

True Spherical Fine Particles: particles mfd. by Dow Chemical Co., U.S.A., trade name: UNIFORM LATEX PARTICLES

Particle sizes are determined by SEM (scanning electron microscope), Dow.

0.085 μm (deviation 0.0055 μm)

0.109 μm (deviation 0.0027 μm)

0.330 μm (deviation 0.0040 μm)

0.806 μm (deviation 0.0057 μm)

2.02 μm (deviation 0.0135 μm)

2.97 μm (deviation 0.23 μm)

Aspect Ratio Calculation

An inorganic laminar compound alone and a resin composition were respectively subjected to diffraction measurement by means of a commercially available X-ray diffractometer (trade name: XD-5A, mfd. by Shimazu Seisakusho K. K.) through a powder method. The lattice spacing (unit thickness) a was determined on the basis of the measurement of the inorganic laminar compound alone. In addition, it was confirmed that a portion in which the lattice spacing of the inorganic laminar compound had been increased (a portion in which lattice spacing $d > a$) was present in the resin composition, on the basis of the diffraction measurement of the resin composition.

By use of the resultant particle size L obtained by the dynamic scattering method, the aspect ratio Z was determined by using an equation of $Z=L/a$.

Example 1

Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo K. K.) was dispersed in ion-exchange

water (electric conductivity: $0.7 \mu\text{S/cm}$ or below) so as to provide a concentration of 2 wt. %, thereby to provide a dispersion of an inorganic laminar compound (Liquid A). The above montmorillonite had a particle size of 560 nm, a unit thickness a obtained by powder X-ray diffraction of 1.2156 nm, and an aspect ratio of 461.

Separately, a polyvinyl alcohol (trade name: PVA 117H, mfd. by Kuraray K. K., saponification degree=99.6%, degree of polymerization=1700) was dissolved in ion-exchange water (electric conductivity: $0.7 \mu\text{S/cm}$ or below) so as to provide a concentration of 2 wt. %, thereby to provide a resin solution (Liquid B).

The thus obtained Liquids A and B were mixed with each other so as to provide a solid content ratio (volume ratio) of (inorganic laminar compound/resin)=3/7, thereby to provide a coating liquid.

A 150 μm -thick poly-3-hydroxybutyrate (trade name: Biopol, mfd. by ICI) was used as a base film and was subjected to corona discharge treatment. Onto the thus treated base film, the coating liquid having the above composition was applied, and then dried at room temperature and further dried at 80°C for two hours, thereby to provide a laminate film. The thickness after drying of the above coating layer was 0.5 μm .

The thus obtained biodegradable resin film had an oxygen permeability of $0.09 \text{ cc/m}^2 \cdot \text{day} \cdot \text{atm}$ at 31°C ., 61% RH (relative humidity), and was found to have an excellent gas barrier property.

On the other hand, the above laminate film was subjected to a biodegradability test. As a result, the production of a large number of pores was observed by naked eyes. The film had a residual area ratio of 55% after two months, and showed an excellent degradability as shown in Table 1 (FIG. 7) appearing hereinafter.

Examples 2-10

Laminate films were prepared and were subjected to an oxygen permeability test, and a biodegradability test in the same manner as in Example 1, except that those constituents thereof were respectively changed to those shown in Table 1. The test results are shown in Table 1 appearing hereinafter.

As shown in the above Table 1, the laminate films obtained by these Examples were excellent both in the gas barrier property and in the biodegradability.

Example 11

Zirconium ammonium carbonate (trade name: Zircozol AC7, mfd. by Dai-ichi Kigenso Kogyo K. K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide)), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising the Liquid A and Liquid B prepared in Example 1 in an amount so as to provide a ratio of the zirconium element of one mole, with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol.

By use of the resultant mixture, a laminate film was prepared and was subjected to an oxygen permeability test, and a biodegradability test in the same manner as in Example 1, except that the constituents thereof were changed to those as shown in Table 1. The measurement results are shown in Table 1 appearing hereinafter.

As shown in the above Table 1, the laminate film obtained by this example was excellent both in the gas barrier property, and in the biodegradability.

Zirconium ammonium carbonate (trade name: Zircozol AC7, mfd. by Dai-ichi Kigenso Kogyo K. K., an aqueous solution containing 15 wt. % of the solute (calculated in terms of zirconium oxide)), as a crosslinking agent for hydrogen-bonding group was added to the mixture solution comprising Liquid A and Liquid B prepared in Example 1 in an amount so as to provide a ratio of the zirconium element of one mole with respect to 15 mole of the hydroxyl group of the polyvinyl alcohol.

By use of the resultant mixture, a laminate film was prepared in the same manner as in Example 1, except that the other constituents were changed to those as shown in Table 1. Thereafter, the resultant laminate film was subjected to a heat treatment by means of a hot-air dryer at 140° C. for 10 min., thereby to provide a laminate film.

The thus prepared laminate film was subjected to an oxygen permeability test and a biodegradability test. As shown in the above Table 1, the laminate film obtained by this Example was excellent both in the gas barrier property and in the biodegradability.

Comparative Examples 1-3

Films were prepared and wire subjected to an oxygen permeability test, and a biodegradability test in the same manner as in Examples 1-3, except that a layer comprising a resin composition comprising an inorganic laminar compound and a biodegradable resin was not disposed. The test results are shown in Table 1.

As shown in the above Table 1, the films obtained by these Comparative Examples were considerably poor in the gas barrier property.

Comparative Example 4

A films was prepared and was subjected to an oxygen permeability test, and a biodegradability test in the same manner as in Examples 1-3, except that the dispersion of the inorganic laminar compound (Liquid A) used in Example 1 was not used. The test results are shown in Table 1.

As shown in the above Table 1, the film obtained by this Comparative Example was poor in the gas barrier property.

Comparative Example 5

A 60 μ m-thick polyethylene film was prepared and was subjected to an oxygen permeability test. The test results are shown in Table 1.

As shown in the above Table 1, the above polyethylene film was considerably poor in the gas barrier property and in the biodegradability.

The meanings of the abbreviation used in the above Table 1 (FIG. 7) are as follows.

PHB: poly-3-hydroxybutyrate trade name: Biopol HVO %, mfd. by ICI)

HBHV4: 3-hydroxybutyrate (96%)-3-hydroxyvalerate (4%) copolymer (trade name: Biopol HV4%, mfd. by ICI)

HBHV9: 3-hydroxybutyrate (91%)-3-hydroxyvalerate (9%) copolymer (trade name: Biopol HV9%, mfd. by ICI)

CHI: Water-soluble chitin (A product obtained by about 50%-deacetylating a product "Chitin" (mfd. by Nakarai-tesque Co.) in a manner as described in a paper (T. Saran et al., *Makromol. Chem.*, 177, 3589 (1976)), cast film

CHIT: Chitosan (mfd. by Nakarai-tesque Co.), cast film
PUR: Pullulan (mfd. by Nakarai-tesque Co.), cast film

LDPE: A low-density polyethylene film product obtained by subjecting a polymer (trade name: Sumikathene F208-C mfd. by Sumitomo Chemical Co., Ltd.) to inflation shaping at 180° C.

F: Natural montmorillonite (trade name: Kunipia F, mfd. by Kunimine Kogyo Co.)

H: Polyvinyl alcohol (trade name: Poval 117H, mfd. by Kuraray K. K.)

Z: An aqueous solution of zirconium ammonium carbonate (trade name: Zircozol AC7, mfd. by Dai-ichi Kigenso Kogyo Co.)

FIGS. 8-13 respectively show powder X-ray diffraction peaks of inorganic laminar compound and composition having various values of the lattice spacing d.

FIG. 8 is a graph showing X-ray diffraction peaks of a polyvinyl alcohol PVA-117H/"Kunipia F" composition used in the above Examples. FIG. 9 is a graph showing X-ray diffraction peaks of "Kunipia F" (montmorillonite) used in the above Examples.

FIG. 10 (composition having a lattice spacing $d=19.62 \text{ \AA}$ (pattern of the above FIG. 2), FIG. 11 (composition having a lattice spacing $d=32.94 \text{ \AA}$ pattern of the above FIG. 2 or FIG. 3), FIG. 12 (composition having a lattice spacing $d \geq 44.13 \text{ \AA}$, pattern of the above FIG. 3), and FIG. 13 (composition having a lattice spacing $d \geq 44.13 \text{ \AA}$, pattern of the above FIG. 3) are graphs respectively showing powder X-ray diffraction peaks of compositions having various values of the lattice spacing d.

Industrial Applicability

As described hereinabove, the present invention provides a resin composition, a film, or a shaped article having a good gas barrier property, while substantially retaining the biodegradability thereof.

When the resin composition according to the present invention is formed into a film shape, it is suitable for use as a packaging material which is inclusive of: packaging for foods such as: "miso" (soybean paste), dried bonito, confectionery, Chinese noodles, ham, sausage, retorted foods, and frozen foods inclusive of croquette; and packaging for other contents such as chemicals or medicines, and precision materials. In addition, the resin composition according to the present invention is suitably usable as a shaped article in the form of bottle, tray, etc., to be used for a squeezing-type bottle of mayonnaise, juice, soy sauce, edible oil, sauce, food tray for microwave oven, cups for yogurt, etc.

The resin composition according to the present invention may exhibit a good biodegradability in any form or shape of those as described hereinabove. As a result, the present invention may considerably contribute to the maintenance or protection of a terrestrial environment such as the disposal of trash or rubbish, or plastic wastes; and reduction in the amount of wastes in a landfill.

What we claim is:

1. A biodegradable resin film having at least two layers having:

a first biodegradable layer comprising the composition which comprises:

a biodegradable resin which is capable of being biodegraded by the action of a microorganism, said biodegradable resin is a hydrogen-bonded resin wherein said hydrogen-bonded resin has 10% to 60% by weight of hydrogen-bonding groups selected from the group consisting of hydroxyl groups, amino groups, amide groups and thiol groups, and an inorganic laminar compound having aspect ratio (Z) of from 100 to 3000, wherein the aspect ratio (Z) is

defined by the equation $(Z)=L/(a)$, wherein L represents the particle diameter of the inorganic laminar compound measured in a solvent by a dynamic light scattering method, and (a) represents the unit thickness of the inorganic laminar compound measured by powder x-ray diffraction, and wherein said inorganic laminar compound is swollen or cleft in a solvent; and

a second biodegradable layer comprising a material selected from the group consisting of polyester poly-3-hydroxybutyrate, 3-hydroxybutyrate-3-hydroxyvalerate copolymers, chitin, and chitosan.

2. A biodegradable resin film according to claim 1, wherein the composition has a relative ratio of the integrated intensity of the standard diffraction peak corresponding to the lattice spacing a to that of the diffraction peak corresponding to the lattice spacing d of 2 or more, wherein both the diffraction peaks are observed in the powder X-ray diffraction of the resin composition.

3. A biodegradable resin film according to claim 1, wherein the biodegradable resin is a resin comprising a polyvinyl alcohol or a polysaccharide as a main component.

4. A biodegradable resin film according to claim 1, wherein the inorganic laminar compound is an inorganic laminar compound having a particle diameter of 5 μm or smaller.

5. A biodegradable resin film according to claim 1, wherein the inorganic laminar compound comprises a clay mineral having a swelling property.

6. A biodegradable resin film according to claim 1, wherein the biodegradable resin comprises a polyester producible by a microorganism as a main component.

7. A biodegradable resin film according to claim 1, wherein the biodegradable resin comprises a biodegradable polyester as a main component.

8. A biodegradable resin film according to claim 1, wherein the biodegradable resin film has, an oxygen permeability of not more than 0.2 cc/m²·day·atm under the conditions of 30° C. and 60% RH (relative humidity).

9. A shaped article comprising a biodegradable resin film according to claim 1.

10. A biodegradable resin film according to claim 1, wherein the biodegradable resin is poly-3-hydroxybutyrate or 3-hydroxybutyrate-3-hydroxyvalerate copolymer.

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